



# Modern Methods of Refining LUBRICATING OILS

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## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie*, Moissan's *Traité de Chimie Minérale Générale*, Friend's and Mellor's *Textbooks of Inorganic Chemistry* and Heilbron's *Dictionary of Organic Compounds*, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important

service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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## PREFACE

The last few years have witnessed radical changes in the methods of refining and manufacturing lubricating oils. The conventional sulfuric acid treating and naphtha dewaxing processes are now gradually being displaced by the newly developed solvent processes, while the use of additives for improving certain particular characteristics of petroleum products are beginning to assume an increasingly greater commercial importance. Until recently these new refining methods had not yet been sufficiently clarified and standardized, and the available information has been inadequate for presenting a generalized discussion on the subject. By now, however, many of the controversial aspects of the solvent refining processes and their commercial applications have been, to a greater or less extent, clarified and have made possible the publication of the present volume.

The primary object of this book is the systematization of our knowledge on the modern methods of refining, and classification of the numerous processes proposed in the course of the last few years for commercial use. The discussion is restricted, however, only to the general principles underlying these refining methods and to the description of the processes which have found actual commercial applications. The literature and patent references nevertheless were made as complete as possible in order to facilitate an evaluation of the relative merits of the various proposed substitutes and of their proper location in the general scheme of refining.

In the description of various processes it will be noted that dewaxing methods are discussed prior to deasphalting methods, while in practice deasphalting usually precedes dewaxing. Such an arrangement has been found, however, to facilitate the presentation of the subject matter covered in this book.

The writer wishes to express his gratitude to Dr. A. B. Brown and others of the staff of the Standard Oil Co. of Indiana, and to Dr. A. N. Sachanen for their valuable technical criticisms of the manuscript and to Mr. T. A. Petry for his collaboration in preparing the chapter on theoretical principles of the solvent refining processes; to Dr. J. B. Rather, in charge of the General Laboratories of the Socony-Vacuum Oil Co., Inc., and the late Dr. D. P. Weld, formerly in charge of the Research and Development Division of the Socony-Vacuum Oil Co., Inc., for per-

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# MODERN METHODS OF REFINING LUBRICATING OILS

## Chapter I

### Properties of Refined Oils

Constant increase in the application of mineral oils in a variety of technical problems has resulted in the development of a large number of commercial products satisfactorily performing under many service conditions. These oils of necessity must meet different specifications. Much ingenuity is frequently required of petroleum refiners in the development of new grades of finished oils or the improvement of the old. Complications are further increased by the difficulty of obtaining reliable results in long-time service tests which are usually difficult to reproduce. The short laboratory methods often lack correlation with the service tests, and, not infrequently, a refined oil must meet specifications which, in the opinion of individual refiners, may either be of no value or even harmful to the customer. A large staff of research chemists is, therefore, employed by many of the oil companies in order to obtain satisfactory products, and it is usually advisable to place more reliance on the reputation of a given concern than on the actual laboratory testing of oils.

Since the primary object of petroleum refining is the preparation of products which will give a satisfactory performance and be acceptable to the trade, a general discussion of the present methods of evaluating oil quality should precede the description of refinery procedures. The methods discussed below are those which are most frequently encountered in refinery practice.

#### Viscosity Index

One of the major requirements of motor oils or other mineral oil products is their satisfactory viscosity-temperature characteristics. These are necessary in order that the oils will not lose their fluidity but will show an equally good performance through a relatively wide temperature range to which they may be exposed in service. The wider the possible temperature variations, the smaller should be the change in viscosity with temperature. This will insure equal distribution of oil throughout the engine and avoid the possible wear of the moving parts before the engine warms up to its normal running condition. High viscosity at low temperature restricts the flow of the oil when the engine is cold,

while too low a viscosity at the operating temperature may not leave a film of thickness sufficient to prevent metal to metal contacts. An unduly high viscosity also results in large power consumption due to increased friction, although the oil consumption will be less with high viscosity oils than with low viscosity oils. The actual adjustment of oil viscosity, evidently, depends on the specific engine design, but in general it is preferable to use an oil of lower viscosity than that required by specifications.

For oils which are employed at approximately constant temperatures, such as turbine oils, the viscosity-temperature characteristics are of very little or no importance, and the controlling factor is the viscosity at the exact service temperature conditions. The viscosity-temperature specifications for these types of products are, therefore, usually omitted.

The viscosity-temperature characteristics of mineral oils can be estimated over a wide temperature range from viscosity determinations at two different temperatures by employing the viscosity-temperature chart of the American Society for Testing Materials.<sup>1</sup>

A supplementary chart has been developed by Grosholz,<sup>2</sup> which may be frequently of assistance in simplifying certain viscosity calculations. The A.S.T.M. chart is discussed by Graves, Mougey, and Upham;<sup>3</sup> Konheim and Larson;<sup>4</sup> and van Voorhis.<sup>5</sup> The chart is based on the following general equation:

$$\log \log (KV + 0.8) = A + B \log T$$

where  $KV$  is kinematic viscosity in centistokes,  $T$  = absolute temperature and  $A$  and  $B$  are constant.

This method is not convenient, however, for classification purposes as it does not permit an easy visualization of the temperature-viscosity characteristics of an oil in simple numerical units. For these reasons the arbitrary method of expressing these characteristics in terms of the viscosity index numbers has been proposed by Dean and Davis,<sup>6</sup> and is now widely used by the oil industry due to its simplicity. In developing this system, viscosities of two oils were carefully determined at 100° F. and 210° F. in Saybolt Universal seconds. One of these oils had a small viscosity-temperature coefficient (Oil *L*) and the other a large coefficient (Oil *H*). Representative Pennsylvania and Coastal stocks were respectively chosen as the practical extremes at the time the system was developed. In order to make the viscosity index approximately constant for all fractions of a given crude the following procedure was adopted. The relation between the viscosities of 100° F. and 210° F. for individual fractions of Oils *L* and *H* was established by means of the equations:

*Oil having the smallest viscosity-temperature coefficient:*

$$SUV_{100^\circ \text{ F.}} = 0.408 (SUV_{210^\circ \text{ F.}})^2 + 12.568 (SUV_{210^\circ \text{ F.}}) - 475.4$$

*Oil having the largest viscosity-temperature coefficient:*

$$SUV_{100^\circ \text{ F.}} = 0.216 (SUV_{210^\circ \text{ F.}})^2 + 12.07 (SUV_{210^\circ \text{ F.}}) - 721.2$$

where  $SUV$  is the Saybolt Universal viscosity at 100° F. and 210° F.

The oil having the smaller coefficient (Oil *L*) was assigned a viscosity index of 100, and the oil with the larger coefficient (Oil *H*) a viscosity index of 0. The viscosity index of an unknown sample of oil (Oil *U*) is determined by substituting its viscosity at 210° F. in the above equations and by determining the viscosities of Oils *L* and *H* at 100° F. which have the same viscosity at 210° F. as the unknown sample. The viscosity index is then calculated from the equation:

$$\text{Viscosity index} = \frac{V_L - \bar{V}_U}{V_L - V_H} \times 100$$

where:  $V_L$  viscosity at 100° F. of 100 viscosity index oil

$V_H$  viscosity at 100° F. of 0 viscosity index oil

$V_U$  viscosity at 100° F. of the sample.

These calculations can be simplified by the use of alignment charts,<sup>7</sup> or tables such as the ones included in the appendix (Table 3).

Docksey, Hands, and Hayward<sup>8</sup> developed equations and charts which permit calculations of the viscosity indexes from kinematic viscosities. McCluer and Fenske<sup>9</sup> developed conversion factors for expressing kinematic viscosities in terms of Saybolt viscosities, and Hersh, Fisher, and Fenske<sup>10</sup> worked out the necessary tables for estimating the "kinematic viscosity index" on the basis of their careful viscosity measurements of the representative oil fractions.

The above equations were developed for oils which have a viscosity not less than 45 and not more than 160 Saybolt Universal seconds at 210° F. For the very light oils the experimental error in determining Saybolt viscosities is very great in comparison with the total spread between the two standard oils of 0 and 100 viscosity indexes and absolute viscosities should, therefore, be employed for calculating the Saybolt viscosities to be used in the equations. Oils of viscosities above 160 seconds at 210° F. were not investigated by Dean and Davis and the extrapolations into these viscosity index regions are, therefore, unreliable.

Several attempts have been made to extend the viscosity index range beyond the above viscosity limits, as well as to change the formulas recommended by Dean and Davis. It is, therefore, always desirable to specify the system which is adopted for calculating the viscosity index. In this book the system of Dean and Davis is used throughout as the one most generally accepted.

The approximate viscosity index of unrefined lubricating oil fractions obtained by distilling typical crudes is given in the following table:

TABLE 1—Viscosity Index of Lubricating Oil Fractions

|                     |     |
|---------------------|-----|
| Gulf Coast .....    | 0   |
| Peruvian .....      | 20  |
| Columbian .....     | 40  |
| East Texas .....    | 60  |
| Mid-Continent ..... | 80  |
| Pennsylvania .....  | 100 |

It should also be noted that the viscosity index is not an additive quantity and that blends of very light oils, with heavy residuums of the same viscosity index may in some instances have a higher viscosity index than either of the two components and usually a higher viscosity index than the arithmetical average of the two components. There seems to be little practical reason for estimating viscosity indexes with an accuracy greater than within five or even ten units for very light products unless extreme precautions are taken in viscosity measurements.

Besides expressing the viscosity-temperature relationship, the viscosity index may also be employed for estimating molecular weights of oils when extreme accuracy is not required. For this purpose, Fenske, McCluer, and Cannon<sup>11</sup> recommend the following empirical formula:

$$\text{Molecular weight} = 240 + \frac{32,310 \log_{10} \frac{SUV_{100^\circ \text{ F.}}}{28.0}}{305 - \text{viscosity index}}$$

which is claimed to be accurate to within 2%. This shows that changes in the viscosity index in refining have more than just purely physical significance.

A variety of other methods for expressing the viscosity-temperature relationship of lubricating oils has been proposed but up to the present time these methods have not found wide acceptance. Wilson and Barnard<sup>12</sup> suggested using the ratio of viscosities at 100° F. and 210° F. Bell and Sharp<sup>13</sup> recommend the use of the slope of the viscosity-temperature line on the A.S.T.M. chart which is calculated from a special scale superimposed on this chart. McCluer and Fenske<sup>14</sup> employ the ratio of viscosity of a given oil at 0° F. to that of a reference oil of equal viscosity at 210° F. Nevitt<sup>15</sup> uses the tangent or the angle of slope of the viscosity line on the A.S.T.M. chart. Clayden<sup>16</sup> introduced the conception of the viscosity gradient which is defined as the viscosity in centistokes which the oil would have if its viscosity at 0° F. were 10,000 centistokes. Larson and Schwaderer<sup>17</sup> recommend a modified viscosity index scale by dividing the scale into eight equal zones of which each is made equal to 12½ viscosity index numbers. This has the advantage of minimizing the delicacy of the scale which is frequently beyond the accuracy of the actual viscosity measurements and loses its practical significance.

### Viscosity-Gravity Constant

Viscosity-gravity constant is sometimes employed instead of viscosity index for expressing those changes in the chemical composition of the oil, bearing particularly on the temperature-viscosity characteristics, which are brought about by refining processes. This constant was originally developed for classification of crude oils.<sup>18 \*</sup>

Although the inventors of this constant cautioned against its application to semi-refined or refined products, it is frequently employed as a substitute for viscosity index. It is so used particularly for oils of low

\* A very convenient alignment chart for calculating this constant has been prepared by Houghton and Robb.<sup>19</sup> Another similar chart was also developed.<sup>20</sup>

viscosity, the viscosity index of which cannot be conveniently determined with the required accuracy. The mathematical relationship for the viscosity-gravity constant is as follows:

$$a = \frac{10G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}$$

where:

$a$  = viscosity-gravity constant,  
 $V$  = Saybolt Universal viscosity at 100° F.  
 $G$  = specific gravity at 60° F.

or

$$a = \frac{G - 0.24 - 0.022 \log (V' - 35.5)}{0.755}$$

where:

$V'$  = Saybolt Universal viscosity at 210° F.

The viscosity-gravity constant is based on the well known relationship that the paraffinic oils exhibit a low specific gravity, and the naphthenic oils a high specific gravity for any given viscosity and is, therefore, a useful indication of the source of a given crude. As the naphthenic oils have a low viscosity index, and the paraffinic oils have a high viscosity index, attempts have been made to correlate the viscosity index with viscosity-gravity constant and to apply such correlations to refined oils.

The following data on four typical but untreated lubricating oils were presented by Ferris and Houghton<sup>21</sup> to show the correlation between the viscosity-gravity constant (V.G.C.) and the viscosity index (V.I.). McCluer and Fenske<sup>22</sup> recommend the use of gravity index, which was selected so that gravity index numbers, which are functions of the viscosity-gravity constant, become similar to viscosity index numbers for the same oils. See also a correlation between viscosity-gravity constant and viscosity index.<sup>23</sup>

TABLE 2—Relation Between Viscosity-Gravity Constant and Viscosity Index

| Type of Crude            | V.G.C. | V.I. |
|--------------------------|--------|------|
| Pennsylvania .....       | 0.812  | 105  |
| Mid-Continent .....      | 0.846  | 72   |
| Gulf Coast .....         | 0.885  | 18   |
| Extreme Gulf Coast ..... | 0.935  | 145  |

This should usually be avoided, however, since possible deviations may be well above the permissible limits of accuracy. Thus Michigan (Mt. Pleasant) residuum solvent refined to a viscosity-gravity constant of 0.863 has a viscosity index of 104, and when solvent refined to a viscosity-gravity constant of 0.818 it has a viscosity index of 125. Nevertheless the viscosity-gravity constant is very helpful in controlling plant production on known oils or in attempting to investigate the effect of solvent refining on oil fractions the viscosity of which is beyond the viscosity index range.

### Boiling Point and Optical Indexes

Besides viscosity index and viscosity-gravity constant, the viscosity-boiling point constant and the corresponding boiling point index were also developed.<sup>18</sup> \* This boiling point index employs the relationship between the viscosity of the oil and the 50% boiling point (at 10 mm. Hg. pressure) of the fraction as the naphthene base oils have a lower boiling point for a given viscosity than the paraffin base oils. The optical index or the refractive index-viscosity constant is now also in the state of development.<sup>25</sup> †

The above indexes are based on change of physical properties due to change in relative proportions of the several types of chemical structures making up the oil, but none of them has what might be termed a scientific interpretation. The numerical values of these indexes for a given oil are also not necessarily the same, particularly with solvent refined products.

### Carbon Residue and Carbonization Index

Carbon residue or Conradson carbon<sup>27</sup> and coke number or Ramsbottom carbon<sup>28</sup> are frequently used for estimating the carbonizing properties of lubricating oils in engines. In these tests, oil is vaporized at atmospheric pressure by application of heat, and the residue weighed and expressed as percentage of the charge. The coke number is easier to reproduce than the carbon residue as it is better standardized by using a somewhat more elaborate equipment. The coke number is usually lower than the carbon residue of the same oil although no general correlation between these two methods appears to exist.

Better correlation between the results of laboratory and engines tests are apparently obtained by measuring the carbonization index of the oil which is defined as the temperature of the 90% distilled point at an absolute pressure represented by 1 mm. mercury.<sup>29</sup>

However, although it is true that the above tests may be of value in comparing oils of similar origin which have received a similar treatment, they lose their practical significance when comparisons are made of oils coming from different sources or subjected to different treating procedures.<sup>30</sup>

This is due to the differences in the characteristics of the carbon formed in the engine. Some types of carbon are rather fluffy in character and thus easily eliminated through the exhaust, while others form a hard film on pistons or on cylinder walls. It is also debatable whether an oil with an exceptionally low carbon residue or coke number is desirable, since a slight carbonaceous deposit may be of some value in pro-

\* Alignment chart was developed by Jackson.<sup>24</sup>

† Fuchs and Anderson<sup>20</sup> use specific dispersion method for similar purposes.

tecting the oil from direct action of the metal. These questions are, however, not yet definitely settled.

### Color

Although it is generally agreed that the color of the oil has little relation to its quality, it still appears in trade specifications and is, therefore, of importance. The consumer also frequently demands that the oils have the fluorescence or "bloom" characteristic of Pennsylvania oils. The color of the oil is measured by comparing it with certain standards by using transmitted light. A variety of colorimeters have been proposed for measuring colors of petroleum oils and can be classified in several different ways:

1. By the method of taking observations: human eye or mechanical device (photoelectric cells).
2. By the method of matching colors: variable or fixed thickness of the oil layers with the respective fixed or adjustable standard.
3. By the method of illuminating the instrument: artificial or sunlight, white or monochromatic light.
4. By the method of defining standard colors: colored glass discs, colored solutions, intensity of color without reference to hue, or hue without reference to the intensity of color.
5. By the method of expressing the results: arbitrary scales or approximations of additive or "true" color scales.

Of commercial instruments, Union Colorimeter,<sup>31</sup> Tag-Robinson Colorimeter,<sup>32</sup> Lovibond Tintometer,<sup>33</sup> as well as Saybolt Chromometer<sup>34</sup> are most frequently used in this country, while Wilson's Chromometer,<sup>35</sup> Hellige Colorimeter,<sup>36</sup> and Stammer's Chromometer,<sup>37</sup> are often referred to in Europe.

The difficulty of developing a satisfactory system of color measurements lies in the complexity of analyzing it in simple units. The color is perceived by the eye as a single sensation, but it might be considered to possess three distinct attributes: hue, by virtue of which the color differs from gray and which is specified by the wave-length; saturation, which is defined as the degree of purity, or freedom from wave-lengths other than the principal one, and brilliance, which classifies the color, irrespective of its hue or saturation, as an equivalent of some number of a series of grays ranging from black to white, and which is frequently designated in petroleum work by its reciprocal-color intensity. Commercial instruments attempt to express the color in arbitrary units as the color standards and only seldom match the actual color of the oil. For this reason, in comparing colors, it is left to the operator to determine which one of the above attributes is the most important. Consequently,

the color reported is in reality only an individual interpretation which is open to disagreement.\*

Attempts are now being made to develop instruments which would measure only one of the color attributes but in a quantitative way. The photoelectric colorimeters<sup>39</sup> are in this respect of considerable value because they express in exact and reproducible units the brilliance (or color intensity) of the oil, while the use of monochromatic light<sup>40</sup> gives a more or less close approximation of the hue.

### Fluorescence

Fluorescence is usually measured by inspecting the oil sample in reflected light because no commercial instruments are yet available for expressing it in some definite units.†

Fluorescence is apparently due to the presence of some particular forms of highly polymerized molecular structure, possibly of colloidal nature, which are capable of reflecting the light from the surface of the oil. A well refined oil from which such substances are removed, therefore, possesses little or none of this fluorescence and is somewhat dull in appearance. Due to its transparency the small quantities of carbonaceous material formed in the engine are easily visible, and the consumer is apt to think that the oil is deteriorating rapidly in use although the actual amount of sludge present is negligible. Oils possessing fluorescence, on the other hand, may contain very appreciable amounts of sludge and still appear clear thus deluding the observer.

The above shows that fluorescence or "bloom" has no significance as an index of the performance characteristics of an oil. The present trade requirements for oils having the yellowish-green fluorescence associated with Pennsylvania stocks should be, therefore, regarded as a relic of the past of no value to the customer.

The yellowish-green fluorescence of Pennsylvania oils is obtainable commercially on stocks from other crudes by several methods, notably, high temperature clay contacting, by deasphalting and acid treating in propane solution, by addition of suitable dyes, etc. These methods are described in more details in the succeeding chapters.

### Oxidation Stability

Oxidation stability is considered a very important characteristic of an oil. It is usually measured by the change in the properties of the oil such as carbon residue or coke number or quantity of sludge formed, viscosity, color, and neutralization number, on oxidation. Some tests measure only one of such properties while others take into account the

\* Lederer<sup>38</sup> employs a formula for expressing the color of an oil as a function of both hue and color intensity.

† Evers<sup>41</sup> recommends an instrument for measuring fluorescence employing a step photometer.

change in several of them. A variety of oxidation tests were thus developed (Table 6, Appendix). Some of these tests are particularly suitable for motor oils (Indiana oxidation test, Socony oxidation test, and the Sligh test, which is of more importance to light distillate oils than to heavy products), airplane engine oils (British Air Ministry test as well as tests applied to motor oils), transformer and turbine oils (German Tar Number test, Michie test, Belgian test, Brown-Boveri Transformer oil test, Brown-Boveri Turbine oil test), etc. The large variety of these tests shows in itself that none of them guarantees the perfect performance of an oil in service. It is likewise not infrequent that results obtained with one of such tests are in direct contradiction with the results of another test of similar nature. Thus the German Tar Number increases while the quantity of sludge formed in the Michie test decreases with the depth of refining. In general, however, the closer the test approaches the actual conditions in the engine the more reliable are the results, but this requires the use of relatively low temperatures and long periods of time thus depriving the research worker of the benefit of accumulating experimental data at the required rate of speed. Many of the above tests employ catalysts which are usually chosen from metals of which the engine is built. This tends to approach more closely the practical conditions.

The oxidation stability of a motor oil should be, evidently, high, particularly if the engine is equipped with oil filters, in which case the oil remains in use for a long period of time and is only seldom changed. It is of less importance whenever the oil changes are frequent.

### **Pour and Cloud Points**

The solidifying characteristics of the oil should be low so as to insure good lubrication as soon as the engine is started. It is measured by the cloud and pour point test,<sup>42</sup> \* cold test,<sup>44</sup> or other similar tests. These tests are performed under exactly specified conditions since the change in the shape or volume of the vessel, heating of the sample before testing, the quantity of the oil used, rate of chilling, etc., influence considerably the results. An oil which will not flow in a small container may be quite fluid when a large container is used. In general the high pour test oil is not necessarily associated with the difficulty of starting the engine, but it is undesirable as the flow of such oil from the oil sump to the pump intake is unsatisfactory. This results in the excessive wear of moving parts before the oil is sufficiently heated. On the pressure side of the system the flow will usually be satisfactory even with a relatively high pour test oil, provided the pump can "take suction."

\* See also criticism of the test by Moerbeek and Van Beest.<sup>43</sup>

### **Flash and Fire Points**

The flash and fire points are usually given in specifications. The flash point is considered to be an indication of the presence of very small quantities of substances which are more volatile than the main body of the oil while the fire point is believed to indicate the temperature at which the major portion of the oil begins to vaporize. These are indirect measures of the volatility of an oil and may serve as indication of the oil source because for equal viscosities and widths of the fractions a Pennsylvania oil has higher flash and fire points than Mid-Continent and particularly Coastal stocks.

By proper fractionation an oil can be obtained which has a very high flash point for a given viscosity as compared with that produced by less careful fractionation (Stratford, Moor, and Pokorny).<sup>45</sup>

While flash and fire points are of practical significance for certain types of petroleum products such as transformer oils, etc., in an engine they are lowered at once as the fresh oil is introduced and mixed with the heavy gasoline fractions that accumulate in the crank-case due to their incomplete combustion. The flash and fire points may have a certain bearing, however, on other oil properties such as oil consumption in the engine, etc.\* In general, removal of asphalt from an oil tends to decrease slightly its flash and fire points while the removal of wax may raise them by a few degrees. This may be frequently attributed, however, to the removal of the light portions of an oil in distilling off the dewaxing solvent.

### **Effect of Various Oil Constituents on Oil Properties**

The effect of refining on other oil properties will be discussed in more detail in connection with the specific refining processes. It might be stated in general, however, that removal of wax from the oil increases its specific gravity and viscosity and lowers the viscosity index. Removal of asphalt decreases the specific gravity and viscosity while the viscosity index frequently remains unchanged or is even lowered. Elimination of low viscosity index constituents in solvent refining lowers the specific gravity and viscosity of the oil and improves the viscosity index. These changes are important for the refinery in order to select the crude oil fraction which is required for preparing the desired grade of finished oil.

In general, the above discussion bears out the unreliability of the present laboratory testing methods, the significance of which should never be over emphasized. The final test to which an oil is subjected should always be performed in an engine. As engine tests are difficult to reproduce on account of many variables present, a large number of them

\* Volatility appears to be directly related to the oil consumption in an engine (Davis and Best,<sup>46</sup> and Danse<sup>47</sup>).

should be made so as to obtain reliable averages before the product is placed on the market.

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## Chapter II

### Modern Refining Methods

The general object of lubricating oil refining is the improvement of oil properties and rendering oil suitable to service conditions. Oil properties can be improved, however, in a variety of ways which may be classified as follows:

1. Elimination of the undesirable constituents from the crude products.
2. Rendering the undesirable constituents harmless or even beneficial by neutralizing their action through the introduction into the oil of various inhibitors and similar protective substances, and
3. Converting the undesirable constituents into desirable ones by changing their chemical structure through hydrogenation, condensation or other chemical processes.

The first two methods are described in the succeeding chapters while the third method cannot be considered as a true refining process and is, moreover, only in limited practical use, except in countries deficient in oil resources which, for various reasons, are anxious to maintain their economic independence.\*

It is to be expected, however, that with the exhaustion of our present oil resources this third method of improving crude products will everywhere become of increasing commercial importance as the increased value of crude will result in sufficient savings for justifying the additional expense of securing larger yields of refined materials than those obtained by the present refining methods.

#### Relation Between Sulfuric Acid and Solvent Refining Methods

In eliminating the undesirable constituents from crude lubricating oils three major classes of substances are usually considered: asphaltic bodies, wax, and low viscosity index or chemically unstable constituents. It is somewhat doubtful whether the above classes of compounds cover adequately all of the undesirable constituents present in an oil, such as certain types of color bodies, acidic components, etc., but these latter substances are usually eliminated more or less completely in removing the aforementioned major classes of substances and only in exceptional cases present real difficulties to the refiner.

The old conventional refining methods employed sulfuric acid, sodium

\* The fundamental treatises of Ellis<sup>1, 2</sup> completely cover this subject.

hydroxide and clay as the main reagents for removing asphaltic bodies and the low viscosity index or chemically unstable constituents from the crude oils. Of these reagents sulfuric acid was by far the most important one due to its remarkable ability of effectively eliminating most of these undesirable components. The action of sulfuric acid, however, is very complex and is, apparently, both of chemical and physical nature. By modifying the treating conditions it is possible to exercise a certain control over the relative predominance of these two major actions of sulfuric acid, although it is practically impossible to eliminate either one of them completely.<sup>3</sup>

For this reason oils refined with sulfuric acid may contain certain amounts of substances produced in the course of refining, such as sulfonated bodies or products of polymerization and condensation reactions, which are not necessarily of desirable nature. Moreover, the disposal of the acid sludge and the degradation of oil to sludge in the course of refining introduce other undesirable features in the plant operation.

This versatile action of sulfuric acid permits its utilization for the removal of both asphaltic and low viscosity index constituents. However, contrary to the action of sulfuric acid, the new solvent methods are of physical nature only and both the desirable and undesirable constituents are recovered in their original state. These solvent methods are inefficient for separating asphalt from oil. This may possibly be explained by the colloidal nature of the asphaltic particles the removal of which from the oil is, apparently, a colloidal and not a solubility phenomenon. Deasphalting or precipitating agents are, therefore, employed for elimination of asphalt, and sulfuric acid refining is thus substituted by two distinct refinery operations: deasphalting, which is frequently synonymous to distillation, and solvent refining proper.

Elimination of wax from petroleum oils has always been and continues to be a separate refining operation although the development of new dewaxing methods accomplishes the same purposes more economically than before.

### **Classification of Solvent Refining Processes**

From the above discussion it follows that the present refining methods by which the undesirable constituents are eliminated from the oil can be subdivided into deasphalting, solvent refining, and dewaxing methods. However, this classification is not as well defined in practice as some of the reagents employed may exercise more than one action on the oil. Certain deasphalting agents, such as propane or aliphatic alcohols, may exhibit dewaxing properties, while solvent refining agents may remove part of the asphalt, etc. This should be always taken into account in working out proper methods for refining individual oil products in order to obtain the desirable overall balance of refining. It is likewise possible to employ simplified schemes of refining by combining two or more of

the above processes and thus eliminating the necessity of using a large variety of solvents for different purposes. It is thus possible by properly modifying treating conditions to see propane both as a deasphalting and dewaxing agent, benzol—liquid sulfur dioxide as a solvent refining and dewaxing medium, while the deasphalting and solvent refining operations can be likewise carried out simultaneously as exemplified by the Duo-Sol process.

### **Sequence of Solvent Refining Operations**

Assuming the existence of three distinctly different refining processes the question frequently arises as to which is the most desirable sequence of these refinery operations. This problem is primarily of economic nature as the same type of product can be obtained irrespective of whether one of the above processes follows or precedes the other, provided these processes are properly chosen. However, in carrying out any of the above operations the quantity of oil which must be discarded with the undesirable constituents is to a certain extent unaffected by its quality. Thus the oil retained by the wax cake or withdrawn with the asphalt constitutes a certain percentage of the wax or asphalt which depends entirely on the efficiency of the process and not on the quality of the oil. It is, therefore, best to carry out dewaxing and deasphalting operations prior to solvent refining. On the other hand wax tends to concentrate in the raffinate phase and the pour test of the oil is raised in the course of solvent refining when the low viscosity index constituents are separated from the main body of the oil. For this reason the pour point of the oil before solvent refining must be lower than that of the desired pour point of the finished product which can be obtained only by resorting to lower dewaxing temperatures than those required for the oil already refined with solvents. Moreover, the wax obtained from an oil before solvent refining and, particularly, deasphalting operations is more difficult to finish than wax from the deasphalted and solvent refined products. This is obvious as some of the asphaltic and colored bodies are precipitated with the wax and must be removed in the subsequent decolorizing operations. For these reasons, the above questions can be answered only after a thorough study of the individual problems confronting the refiner which must include a careful economic balance of all promising combinations of the individual refinery operations including the finishing costs of the respective products.

### **Finishing of Solvent Refined Oils**

After the oil is refined in the above manner it must usually be finished with clay, or less frequently both with sulfuric acid and clay, in order to obtain marketable products. These finishing procedures are important not only for the purpose of removing additional impurities but also for insuring a uniform refinery product which otherwise may often fluctuate

in its quality, particularly in color, due to irregularities in the preceding operations. The effect of these finishing procedures on the oil quality will be discussed in greater detail later.

### Relative Merits of Sulfuric Acid and Solvent Refining Methods

While the previous discussion was confined primarily to the general outline of solvent refining and allied processes, little was said about the relative merits for the refiner of these modern methods of refining and the old sulfuric acid methods with respect to the improvement in quality of all oil products. As already mentioned, sulfuric acid should be regarded as a reagent which is more universal in its action than solvents. It is not always capable, however, of improving the quality of the oil to the same extent as combined solvent refining and deasphalting operations which, in addition to economic considerations, explains its rapid displacement by the modern refining methods. The general conception of a lubricating oil is usually restricted to the field of motor oils which are evaluated primarily on the basis of their viscosity index, carbon residue and oxidation stability characteristics. Since the solvent refining methods are, generally, superior in this respect to the conventional acid treating methods for improving these particular characteristics of a refined product, there is a tendency to generalize these conclusions and to extend them to all lubricating oils irrespective of their practical applications.

Kalichevsky, Simpson, and Story<sup>4, 5</sup> give the following comparison between the properties of typical high grade motor oils marketed in 1932 and 1937, before and after the introduction of solvent refining processes:

TABLE 3—Typical Motor Oils

|  | 1932           |        | 1937              |        |
|--|----------------|--------|-------------------|--------|
|  | (Acid-refined) |        | (Solvent-refined) |        |
|  | SAE-40         | SAE-60 | SAE-40            | SAE-60 |
| Gravity, deg. API .....                              | 25.7           | 23.7   | 28.8              | 28.0   |
| Pour point, deg. F. ....                             | 20             | 25     | 0                 | 5      |
| Flash point, deg. F. ....                            | 430            | 480    | 460               | 515    |
| Fire point, deg. F. ....                             | 490            | 535    | 520               | 585    |
| Viscosity (Saybolt Universal) at 100° F., sec... 770 | 1,765          | 660    | 1,437             |        |
| Viscosity (Saybolt Universal) at 210° F., sec... 73  | 110            | 73     | 110               |        |
| Viscosity index .....                                | 83             | 80     | 100               | 98     |
| Carbon residue, per cent .....                       | 0.9            | 1.4    | 0.2               | 0.3    |
| Color (Lovibond) .....                               | 170            | 240    | 60                | 80     |
| Slight oxidation No. ....                            | 17             | 4      | 0                 | 0      |

|  | 1932                     |        | 1937                                       |        |
|--|--------------------------|--------|--|--------|
|  | (Percolated and Dewaxed) |        | (Solvent-refined, Percolated, and Dewaxed) |        |
|  | SAE-20                   | SAE-60 | SAE-20                                     | SAE-60 |
| Gravity, deg. API .....                              | 28.4                     | 26.2   | 31.1                                       | 28.5   |
| Pour point, deg. F. ....                             | 5                        | 20     | 0  | 0      |
| Flash point, deg. F. ....                            | 430                      | 510    | 430  | 540    |
| Fire point, deg. F. ....                             | 485                      | 575    | 480  | 610    |
| Viscosity (Saybolt Universal) at 100° F., sec... 373 | 1,736                    | 294    | 1,543                                      |        |
| Viscosity (Saybolt Universal) at 210° F., sec... 57  | 123                      | 55     | 122  |        |
| Viscosity index .....                                | 100                      | 98     | 117  | 105    |
| Carbon residue, per cent .....                       | 0.6                      | 1.5    | 0.3  | 0.4    |
| Color (Lovibond) .....                               | 120                      | 300    | 70   | 30     |
| Slight oxidation No. ....                            | 4.0                      | 1.0    | 0  | 0      |

However, considering the inherent differences between the solvent refining and acid treating processes, it is to be expected that the actual advantages and disadvantages of the two methods may vary depending upon the properties of the oil which must be improved in the course of refining.

Very heavy sulfuric acid treats are capable of yielding oils which, at least in some of their characteristics, resemble the solvent refined products. Thus refining a Mid-Continent residuum of 21.8° API gravity, 150 Saybolt Universal seconds at 210° F., 70 viscosity index (after removing the wax) and 4.3 carbon residue after dewaxing, with one pound of 98% sulfuric acid and 5.4 pounds of fuming acid per gallon followed by contacting with clay and dewaxing to a 10° F. pour test, gave an oil of 30.8° API gravity, 72.2 Saybolt Universal seconds at 210° F., 105 viscosity index and zero carbon residue. Refining of the same residuum with one pound of 98% sulfuric acid per gallon which might be considered as a feasible commercial treat, gave an oil of 25.0° API gravity, 112.5 Saybolt Universal seconds at 210° F., 83 viscosity index and 0.9 carbon residue. The oxidation stability of the sulfuric acid refined products was, however, unsatisfactory as compared to that of the solvent refined products. Moreover losses to sulfuric acid sludge in refining the oil to a 105 viscosity index were tremendous and only a small fraction of the charge could be recovered as finished oil.

In the case of the solvent treating methods, the refining action is of physical nature only. The various constituents of an oil distribute themselves between the two liquid phases formed in such a manner as to result in a concentration of certain materials in the extract or solvent layer, while the remainder of the oil is retained in the raffinate or oil layer. In general, the nature of the materials appearing in the two layers is primarily a function of the temperature of treatment and the relative quantities of solvent and oil present, while the completeness with which those materials are concentrated in the respective layers is governed principally by the method of extraction employed. Under a given set of treating conditions, however, the properties of the solvent refined oil depend solely upon the relative solubility of the various constituents of the oil in the two phases formed during the solvent refining operation.

Consequently, certain inherent relationships exist between the various properties of a solvent refined oil which, apparently, cannot be radically altered by controlling the conditions of extraction. For instance, if a given product should be refined to color specifications only, the solvent refining methods will give a simultaneous improvement in the viscosity index and other properties of the oil irrespective of whether these improvements are or are not of interest to the refiner. Hence in meeting certain definite specifications for a given oil, the solvent treat to which the oil must be subjected automatically determines all other properties of the finished product. As a result such an oil may show an unnecessary degree of improvement not included in the specifications and in some instances such improvement may be even harmful for practical purposes.

For instance, in manufacturing cable oils a product is desired which has a satisfactory stability and a low viscosity index.\* Oil refining will

\* Whitehead and Mauritz<sup>6</sup> discuss stability requirements from good cable oils.

yield a product which is very stable for this purpose, but the improvement in the viscosity index of such an oil which accompanies the solvent extraction for improving its stability is considerable and makes the product less suitable for use than the conventionally refined one. Similarly, when an oil must be treated to color specifications only, sulfuric acid refining is frequently capable of accomplishing it with the minimum expenditure of acid and a small loss of oil, while solvent refining to the same color results in considerably larger losses due to the simultaneous improvement in other properties which are of no interest to the refiner. Thus a Coastal distillate of 2.45 Tag-Robinson color and 64 Saybolt Universal viscosity at 210° F. when treated with 15 lbs. 98% sulfuric acid and neutralized with sodium hydroxide yielded a product of 9.25 Tag-Robinson color at a 9% refining loss. By refining the same stock with solvents employing normal plant conditions to the same 9.25 Tag-Robinson color the loss in refining was as high as 21.5%. Moreover, when an additional improvement in the color of the oil was attempted by clay percolation, the two oils, though of equal color, required different quantities of clay in order to obtain an equal improvement to a 12.5 Tag-Robinson color, the acid refined and neutralized oil requiring less clay than the solvent refined oil. These differences in the refining methods are particularly noticeable with oil distillates which are stored for a more or less considerable length of time before refining, probably due to the formation of color bodies which are more susceptible to sulfuric acid than to solvent treats. The above examples, therefore, indicate that the solvent refining methods should be regarded as relatively inflexible, which is to a certain extent contrary to existing opinions.

The inflexibility of the solvent refining methods is likely to be more pronounced with the modern double solvent systems than in the ordinary single or mixed solvent processes. Double solvent systems are designed to refine asphalt bearing residual stocks in one operation, thus eliminating one more variable which can be altered at the will of the refiner, since with the single or mixed solvent methods a separate deasphalting operation is introduced when refining these types of stocks. The double solvent system employs a solvent refining agent and a deasphalting agent simultaneously and hence the treating conditions required for the solvent refining operation may not coincide with those required for the deasphalting operation. Under such circumstances it might be necessary either to sacrifice certain properties of the oil in favor of others or to select intermediate treating conditions for obtaining a reasonable overall quality of the product.

The above shows that while in preparing certain types of products, notably motor oils, the solvent refining methods are superior to the sulfuric acid methods, the same relationship may not necessarily hold for some of the other oil products. As already shown, it may be possible to treat an oil to color specifications more economically with sulfuric acid

than with solvents, as sulfuric acid can be made to exercise more selective properties towards color bodies than solvents. For this reason, the actual economical advantages or disadvantages of the two refining methods may vary depending upon the degree of refining desired and on the particular properties of the oil which must be improved. Although the solvent refining methods are able to prepare better oils for a majority of purposes, in some instances the conventional sulfuric acid methods may still be of economic value. The choice between the two methods is, therefore, dependent entirely upon the particular needs of the refinery.

The rapid growth of the various types of inhibitors or allied substances for the improvement of the properties of lubricating oils has resulted in the development of new methods of rendering oils suitable to service conditions without removing all of the constituents which are generally considered to be harmful. The substances of this type, which are now available, frequently become of value only when applied to semi-refined or highly refined products. More complete discussion is given in the last chapters of this book. The possibility of applying them to oils introduces, however, additional complications into refinery practice due to the necessity of establishing additional economic balances for the most efficient refinery operations, provided the use of such substances is justified by their behavior in service.

The above discussion shows that the introduction of new refining methods has resulted in additional complications rather than simplifications of refinery operations. It likewise can be expected that new methods will appear in the future which will complicate the refining still further and force the refiner to make further changes in his equipment for successful competition with other modern plants.

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### III

### Types of Waxes Present in Petroleum Oils

\* Russteig<sup>2</sup> discusses effect of distillation on pressability of wax distillates. See also Lederer and Zublin.<sup>3</sup>

similar chemical treatment,\* as it is well known that such treats are frequently indispensable for obtaining the type of crystals suitable for pressing operations. To the writer's knowledge, however, no reliable experimental data have yet been presented which would show that petrolatum can be effectively separated into two distinct portions—wax and inhibitor—and that after such separation the inhibitor could be blended with crystalline wax to yield the petrolatum wax. In carrying out such investigations the crystalline wax separated from petrolatum has been invariably found to be incorporated in the petrolatum as an impurity but not as its true component.

According to another theory two distinct types of waxes are present in petroleum: paraffin waxes associated with the light distillates and petrolatum or ceresin waxes found in the heavy residual stocks.<sup>6</sup>

On distillation, some of the ceresins change to paraffins due to thermal decomposition,\*\* although this transformation is never complete. In the cathode vacuum, however, ceresins can be distilled without decomposition. These ceresins differ from paraffins in having a much higher molecular weight than the paraffins as well as a higher specific gravity and a higher refractive index.† The presence of only a few tenths of one per cent of ceresins changes the properties of paraffins to an extent which becomes very noticeable in pressing and sweating operations.‡ The important property of ceresins is their ability of retaining oil to a much greater extent than that exercised by paraffins.

Summing up our present rather meager knowledge on this subject it appears best to assume that two distinct types of waxes are present in the oil, namely, paraffin wax and ceresin wax, but that the structure of paraffin wax may be modified by the presence of crystallization inhibitors which may or may not always be identical with the ceresins. However, by modifying the structure of paraffin wax by means of such inhibitors the resulting product may approach but not become identical in its properties to that of ceresins.

### Wax Content of Petroleum and Its Products

In the above discussion petroleum waxes were considered as being substances distinctly different from the oil from which they can be quanti-

\* For instance Musselman<sup>4</sup> eliminates "amorphous" wax by treating the oil with aluminum chloride. I. G. Farbenindustrie A.-G.<sup>5</sup> employs for the same purpose antimony pentachloride, etc.

\*\* Lindgren and Malm,<sup>7</sup> and Ward,<sup>8</sup> improve filtering characteristics by partially cracking the paraffin distillate.

† Müller and Pilat<sup>9,10</sup> believe that cyclic compounds may be present in petroleum ceresins instead of saturated paraffin hydrocarbons which are considered to be characteristic of petroleum paraffins.

‡ Higgs,<sup>11</sup> in the very interesting article on utilization of paraffin wax and petroleum ceresin, shows that candles containing 0.2-0.3% of petroleum ceresin are stiffened and do not bend easily.

tatively separated. Many analytical procedures were, therefore, devised for determining the wax content of oils or the oil content of waxes and were adopted by various chemical laboratories.\*

These methods, however, lose much of their practical significance due to the existence of a number of substances which because of their intermediate properties can be classified either as oil or as wax. Such substances, which may be of the type of low molecular weight paraffins or which may possess a mixed structure with more or less predominating paraffinic properties, will not crystallize from the oil when the oil is chilled to moderately low temperatures, but will separate out on further chilling. They are present, for instance, in appreciable quantities in Pennsylvania type of crudes which can be dewaxed to a low pour test only at a considerable loss in the yield of the dewaxed oil. This is illustrated by the following example in which a Pennsylvania pressable wax distillate of 68.6 Saybolt Universal seconds at 100° F., and 75° F. pour test, was dewaxed with benzol-acetone mixtures to various pour tests.

TABLE 4—Pour Tests for Pennsylvania Wax Distillate

| Wax Removed<br>% by Weight | Pour Test of Oil<br>° F. |
|----------------------------|--------------------------|
| 0                          | 75                       |
| 9                          | 30                       |
| 11                         | 20                       |
| 13                         | 10                       |

Usually these substances which may be classified as pseudo-waxes, are not easily separated from the oil by filtration in presence of solvents such as benzol-acetone mixtures, etc., although in presence of harder waxes such difficulties may not occur. Similar difficulties are also encountered in determining the oil content of waxes as press methods fail to remove the oil completely while solvent methods extract some of the lower melting point waxes and make the demarkation line between the oil and wax very indistinct.

It should be also noted that by applying identical conditions of extractions to various petroleum products the pour point of the oil is not necessarily reduced to an equal level. Thus by using, for instance, a solvent composed of 20% acetone and 80% toluol by volume at -20° F. the pour point of a deasphalted Mid-Continent residuum was reduced to +5° F. When the same procedure was applied to a deasphalted Talang-Akar residuum of equal viscosity the pour point of the resulting product was as high as +30° F.

\* Holde<sup>12</sup> employs boiling alcohol, Sachanen<sup>13</sup> uses carbon tetrachloride and petroleum ether, Fussteig<sup>14</sup> recommends a mixture of ether, ethyl alcohol, butanone and phenol, Ravikovich and Shile<sup>15</sup> find that best results are obtained with a mixture of ethyl acetate and alcohol, Heinze and Zwergal<sup>16</sup> prefer blends of chloroform and cresol, etc.

The above discussion shows that the wax content of oils has little significance unless some data are presented which indicate the degree of separation between oil and wax attained in the experimental work. This is usually accomplished by specifying the pour test and preferably also the cloud test of the recovered oil, and penetration, tensile strength or some other characteristic of the wax which is appreciably affected by its oil content.

High cloud test indicates that the oil contains some high melting point waxes which tend to separate from the oil before the oil loses its tendency to flow. Such waxes are frequently encountered in heavy fractions of crudes of Coastal type. These waxes should be removed for improving the appearance of the oil although their actual effect on the pour test and fluidity of the oil are insufficient for rendering the oil unfit for service conditions.

Tensile strength of wax is now being gradually adopted by the industry for characterizing the properties of this product. Espach<sup>17</sup> describes this testing method which consists in determining the load required for breaking a sample of wax under exactly specified experimental conditions, and shows the marked effect of the presence of small quantities of oil in lowering the tensile strength of wax samples. The load is applied at a constant rate and the rate of loading has a considerable influence on the reported value of the tensile strength of the wax. According to the writer's experience it appears better to use conditions of constant loading and to record the length of time required to break the wax sample. The resulting logarithmic plot of time of breaking the sample against the load applied is a straight line which can be conveniently used for characterizing the properties of waxes under examination.

The complete analysis of the wax content of oil will then be represented as a function of the pour test of the recovered oil and the quantity of the "wax" removed, while the analysis of wax for its oil content will be similarly expressed as the function of its penetration or tensile strength and the quantity of the "oil" removed.

In employing the pour test of the oil as a criterion of its wax content another complication may arise, however, with certain type of stocks, particularly of asphaltic nature. The presence of asphaltic substances may have an effect similar to that of wax on the pour test of the oil, and heavy residual stocks may often show only a small change in their pour test even after they are thoroughly dewaxed. Such stocks will show an additional, and frequently considerable, lowering of the pour test after the removal of asphalt. Thus by dewaxing a Mid-Continent residuum of 150 Saybolt Universal seconds at 210° F. with a mixture of benzol-acetone at -10° F. the original pour test of the oil of 80° F. could not be reduced below 20° F. irrespective of the experimental conditions used in these extractions. However, a subsequent deasphalting operation reduced the pour test of the dewaxed oil to below 0° F. The asphalt, however, possesses also some pour point depressant qualities, which are discussed in connection with the pour point depressants, and in certain instances removal of asphalt from the oil may result in raising and not in lowering the pour test.

### Effect of Wax on Oil Properties

As already mentioned, the removal of paraffin wax from oils is accompanied not only by the lowering of the pour test but also by other changes in the characteristics of the oil, such as specific gravity, viscosity, viscosity index, color, carbon residue, refractive index, etc. This can be expected, however, as the properties of oils and normal types of waxes are different. As the specific gravity of wax is lower than the specific gravity of oil of the same boiling range, the specific gravity of the dewaxed product is higher and the API gravity lower than that of the oil before dewaxing.

The viscosity of wax at temperatures above its melting point is lower than that of oil of equal boiling range and the viscosity of the dewaxed oil is, therefore, higher than that of the same oil before dewaxing. The change in viscosity after the removal of wax may be illustrated by the following data showing the change in viscosity of light Mid-Continent distillates after dewaxing.<sup>18</sup>

In very exceptional cases, however, viscosity of the oil may decrease after dewaxing thus indicating that viscosity of the wax might be also higher than that of the corresponding oil fraction. Such decrease in viscosity has been observed, for instance, in dewaxing a heavy distillate oil from one of the German crudes.

TABLE 5—Viscosity Change after Dewaxing

| Pressing Temperature<br>° F. | Viscosity<br>Saybolt Universal Seconds at 100° F. |                |
|------------------------------|---|----------------|
|                              | Before Dewaxing                                   | After Dewaxing |
| + 15                         | 100   | 114            |
| + 8                          | 75  | 82             |
| — 5                          | 66  | 69             |
| — 5                          | 66  | 68             |
| — 6                          | 68  | 74             |
| — 8                          | 70  | 76             |
| — 10                         | 58  | 63             |
| — 18                         | 55  | 57             |

Similar changes are observed also with stocks of higher viscosity than those shown in Table 5. The increase in viscosity is particularly noticeable with oils containing large quantities of asphalt when they are dewaxed with solvents which remove the wax without simultaneous precipitation of the asphalt.

Viscosity index of the dewaxed oil is, generally, lower than that of undewaxed oil but, occasionally, the reverse apparently may be true. In general, in measuring the viscosity index of an undewaxed oil viscosities should be determined at temperatures at which wax is completely molten. With some stocks even the temperature of 130° F. is too low to make the viscosity determinations reliable due to incomplete dissolution of the wax. For this reason, the viscosity index of an undewaxed oil is frequently of doubtful value.

The color of the oil and its carbon residue are heightened after dewaxing as the wax can be considered colorless and having a carbon residue of 0. The effect of the quantity of wax added to the oil on its carbon residue has been thus shown to follow the law of simple dilution represented by the following equation:<sup>19</sup>

$$\frac{C_b}{C_a} = \frac{W}{100} + 1$$

where  $W$  is parts by weight of wax added to 100 parts of original oil,  $C_a$ — the carbon residue of original oil and  $C_b$ — the carbon residue of the oil after adding wax.

The change in the refractive index on separating oil from the wax can be even utilized as an analytical method for determining the oil content of waxes.<sup>20</sup>

### Crystallization of Wax

Paraffin wax is known to crystallize in three different forms: plates, needles and mal-crystalline.<sup>21</sup>

According to one theory the wax can crystallize into these various forms by changing conditions of crystallization, such as viscosity of the medium, rate of cooling, etc., while another theory assumes that the crystal form is an inherent property of the different type of compounds present in the wax and is substantially unaltered, except in detail, by the crystallization conditions. This second theory states further that both needle and particularly the mal-crystalline waxes have marked powers, under the proper conditions, of impressing their forms upon plate waxes.\* A paraffin distillate which can be easily pressed is characterized by plate crystals as in the crystallization process the concentration of oil is so high that the needles are kept in solution until the plates are formed as such. The resulting slack wax, however, has little oil present and plates and needles separate simultaneously. The needle form is then impressed upon plates resulting in a wax cake of good sweating characteristics associated with the needle structure.† Similarly the wax constituents which are associated with the higher boiling lubricating oil fractions have a mal-crystalline structure capable of impressing this structure on other wax constituents. This explains the difficulties encountered in pressing wax distillates containing the so-called "amorphous" wax as already discussed in connection with the ceresin waxes.

The rate of cooling is known to be of great importance to the crystal size although the rate of cooling before the separation of crystals occurs seems to have little if any effect,<sup>26</sup> as well as the rate of cooling after the oil is chilled considerably below a certain optimum temperature.<sup>27</sup> The

\* For further references concerning crystallization of petroleum waxes see Katz,<sup>22</sup> Tanaka,<sup>23</sup> Padgett,<sup>24</sup> etc.

† For a more complete discussion see Ferris, Cowles, and Henderson.<sup>21</sup>

rate of cooling is also of more importance to the size of crystals in the lower than in the higher viscosity distillates and residues.

Tanaka,<sup>28</sup> and Tanaka, Kobayashi, and Arakawa<sup>29</sup> express the velocity of growth of wax crystals by the equation:

$$v = \frac{L}{u} (c - s)$$

where:  $v$  is the velocity of growth,  $L$  a constant depending upon the concentration of impurity, rate of cooling and method of stirring,  $u$  the absolute viscosity of the medium,  $c$  concentration of paraffin, and  $s$  solubility.

An inspection of the wax crystals present in the oil is helpful in drawing conclusions with respect to the behavior of this oil in dewaxing. If crystals are large and well defined the oil may be pressed.\* They cannot be centrifuged, however, as the separated wax is not sufficiently fluid to permit its continuous discharge from the centrifuge unless the centrifuge is equipped with scrapers, a rather recent and not yet common development. They can also be cold settled because they fail to form a complicated network peculiar to crystalline wax. However, the cold settling experiments do not necessarily align with the centrifuge experiments as is frequently believed. If the crystals are exceptionally small the oil cannot be centrifuged because the mass of the crystals is not sufficient to overcome the viscosity of the oil medium in ordinary dilutions.

### Conventional Dewaxing Methods

The first method which has been applied for dewaxing petroleum oils was cold settling of the crude. The crude or its lubricating oil fraction was settled during the winter months in large tanks and the main portion of the wax which crystallized out from the oil was then separated from the upper relatively wax-free layer. As a further development of this method, which was formerly used altogether for dewaxing bright stocks, the oil was diluted with light naphtha, usually about 70% by volume, chilled and settled. This process is unfavorably affected by the presence of moisture in the oil, overheating the oil in the distillation process, faulty acid treatment, and improper rate of cooling as for best results the wax must be present in an "amorphous" rather than in a crystalline state. The viscosity and the specific gravity of the oil solution must be also low so as to permit easy settling of the wax.

The cold settling method was soon replaced by filter pressing and centrifuging of the wax. As already mentioned the wax present in light distillates on chilling crystallizes out in sufficiently rigid and well defined crystals so as to permit their separation from the oil by filtration. The heavy residual stocks on the other hand contain a type of wax which

\* Davis and Campbell<sup>18</sup> describe a laboratory procedure developed for this purpose. It is evident that utmost care must be exercised in carrying out this procedure as the lack of standardization of the method of preparing the crystals will affect their relative sizes and shapes and make the method valueless.

cannot be separated from the oil by filtration and the separation is, therefore, effected by centrifuging. For this reason, in distilling the lubricating oil fractions the crude is divided so as to obtain pressable distillates and a residue which can be dewaxed by centrifuging. A slop cut is sometimes obtained, however, which can be neither filter pressed nor centrifuged and causes many inconveniences in the refinery operation. For the same reason difficulties are frequently encountered in dewaxing overhead cylinder stocks as they contain both crystalline (paraffin) and amorphous (ceresin) types of waxes and are for this reason inconvenient in dewaxing operations.

When wax is removed from the distillate fractions by filtration the oil is chilled first either with or without naphtha dilution depending on its viscosity. Dilution is, evidently, undesirable both because it requires additional distillation for removing naphtha from the dewaxed oil and from the wax and also because the differential between the chilling temperature and the pour test of the product must be higher as some wax is soluble in naphtha used for dilution. Distillates of 70-80, and frequently 100 Saybolt Universal seconds at 100° F., can be dewaxed without dilution; but for distillates of 100-200 seconds, from 40 to 50% by volume of naphtha is required, while for heavier stocks the quantity of naphtha may be raised even to 70%. The rate of chilling down to about 10° F. above the cloud test is apparently of no importance, but further chilling is carefully controlled and is usually about 1-2° F. or, as a maximum, 3-5° F. per hour, until the temperature of the oil reaches 0° F. It seems also that further chilling can be done at a much faster rate without undesirable effects on the filtering characteristics of the wax, but, nevertheless, most of the refiners continue to chill slowly until the oil is chilled to the required temperature. The importance of slow chilling rates within a certain temperature range is explained by the importance of forming relatively large crystals so as to facilitate filtering operation. The chilled oil is then filtered through filter cloth, sometimes in presence of small quantities of filter aid to prevent the wax from forming an impervious mass on the filter cloth. Afterwards the filtration naphtha, if used, is distilled off from the oil, although some refineries may percolate the oil through clay while still in naphtha solution and only then remove the diluent naphtha.

The differential between the pour test of the oil and the chilling temperature is usually about 40-50° F. when naphtha is used for dilution, but may be as low as 5-10° F. when dilution is not resorted to. This is explained by the rather considerable solubility of wax in naphtha which becomes an important factor, particularly in dewaxing oils to low pour tests.

In the centrifuging operation the oil is usually diluted with 60-70% naphtha as the residual stocks are too viscous at low temperatures for centrifuging them without dilution. They are then chilled in the same

way as the distillate stocks and charged to centrifuges. In preparing very low pour test oils the oil is sometimes centrifuged first at a relatively high temperature so as to obtain a product of about 20° F. pour test and the resulting solution is chilled further and recentrifuged so as to eliminate further quantities of wax and lower the pour test to about 0° F. or less. Before the oil is charged to the chillers and diluted with naphtha it may be also pretreated with small quantities of sulfuric acid or clay as this frequently facilitates a more complete separation of oil from the wax.

The dewaxing methods which were briefly described above are now being replaced, however, by the more modern methods of dewaxing which are discussed in the subsequent chapters. These modern methods differ from the older methods principally in the nature of the reagents used and not in the basic principles involved in separating wax from oil though minor changes in the design of the equipment are frequently required for adopting these new reagents to practice. For this reason, the general discussion presented in this chapter applies also to the new dewaxing methods.

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## Chapter IV

### Dewaxing with Filter-Aids

The major disadvantages of the old conventional dewaxing methods described in the preceding chapter lie in the necessity of distilling oils before dewaxing in order to separate the paraffin and the ceresin types of waxes requiring different dewaxing methods for their removal from the oil; in the inability of these methods to remove wax from certain types of distillates such as slop cuts or overhead cylinder stocks; in the necessity of employing high temperature differentials between the required pour point of the oil and the dewaxing temperature; and in the lack of a sharp separation between the oil and wax which results in high oil losses. Moreover, commercial application of these processes is frequently associated with further inconveniences such as the necessity of slowly chilling oil solutions to be dewaxed, the importance of pretreating certain types of oils before dewaxing in order to obtain a reasonable degree of separation between the two phases, etc.

#### Modern Dewaxing Processes

Modern refining methods were devised to overcome the above difficulties and at the same time to effect a saving in the cost of dewaxing. Such saving is usually considerable despite the necessity for installing new equipment and the employment of relatively expensive reagents in comparison with naphtha. These modern methods can be generally classified as those employing filter-aids or their equivalents, and those using solvents other than naphtha. This classification is less pronounced, however, in refinery practice as one operation may combine the application of filter-aids with solvents other than naphtha, etc. The classification is convenient, however, for general descriptive purposes.

Besides the above two major types of processes a few more were proposed which employ principles other than those mentioned above. Electrical precipitation methods, for instance, should be classified separately, but as such methods have not yet gone beyond the experimental stage of development they are only briefly mentioned at the end of this chapter.

#### Filter-Aids

The use of filter-aids for filtering compressible cakes is well known to the chemical industries but only recently have they been applied to

the dewaxing of petroleum oils. In the dewaxing operations filter-aids are generally claimed to serve two different purposes: that of supplying a non-compressible material for obtaining wax cakes of required rigidity to insure good filtering rates, and introducing into the dewaxing medium centers of crystallization for the wax when such filter-aids are added to the oil solution before the wax begins to crystallize. While the first contention is well justified the validity of the second is less clear as on chilling oil solutions, the waxes of higher melting point begin to crystallize before the major portion of the waxy constituents, and should, therefore, provide the required centers of crystallization for the remainder of the wax.

Processes involving the use of filter-aids or allied substances can be subdivided into three groups: those in which solid filter-aids are added to the oil solution, those in which liquid or solid substances are dissolved in the oil solution but crystallize out on chilling, and those in which the oil is treated with various chemicals in order to produce a certain amount of sludge acting in the above manner. These processes are described below in the order mentioned.

A large variety of substances has been recommended for use as filter-aids in dewaxing petroleum oils. These include various types of clays and similar materials, wood pulp or paper stock,<sup>1</sup> cellular filter aids,<sup>2</sup> lampblack,<sup>3</sup> litharge, lead sulfide, lead sulfate and similar materials,<sup>4</sup> ground grain hulls,<sup>5</sup> alkaline silicates,<sup>6</sup> finely divided ice,<sup>7</sup> etc.

The practical use of these filter-aids can be visualized from the following description of the Weir process which is being used commercially by the Tidewater Oil Co. and by the Texas Co.

The Weir process<sup>8</sup> is claimed to give satisfactory results with all grades of petroleum oils ranging from low viscosity paraffin distillates to high viscosity residual cylinder stocks. The oil to be dewaxed is diluted with naphtha in the usual manner, the quantity of naphtha in solution ranging from 40% to 75% depending on the stock used. Heating may be required in order to obtain complete dissolution of the wax. The naphtha generally employed has a 58-59° API gravity, a 150° F. to 380° F. boiling range and 130-150 Saybolt thermo-viscosity at 60° F. though other solvents including propane,<sup>9</sup> benzol-acetone, propylene dichloride, etc.<sup>10</sup> may be employed even to a better advantage than naphtha. In general, solutions of low viscosity at filtering temperatures are desirable in order to increase the rates of filtration, other conditions being identical.

The oil-naphtha solution is chilled to the required temperature which is usually 25° F. to 35° F. below the desired pour point of the oil. No special precautions are taken for insuring slow chilling rates. The chilled solution is then transferred into the mixing tank where it is intimately mixed with the filter-aid introduced directly from the recovery

system.\* The filter-aid is usually "Hyflo Super Cel" or "White Speed Flow." The quantity of the filter-aid used varies with the type of stock and the nature of the filter-aid and may be as high as 15% by weight of the oil used.

The resulting mixture is filtered using pressure or vacuum type filters, but the use of centrifuges has also been recommended.<sup>12</sup> Filtering rates usually vary between 0.3 to 1.0 gallon of dewaxed oil per square foot of filtering area per hour. The wax cake is washed on the filters with cold solvent, dried with cold inert gas, and the filter-aid is then recovered by dissolving the deposited wax in hot naphtha. The recovered filter-aid gives the rates of flow which are about 50-60% of those of the new filter-aid, but this lowered efficiency is claimed to remain unaltered irrespective of the number of regenerations.

Fussteig<sup>13</sup> discusses the possibility of recovering paraffin from fuller's earth used in treating lubricating oils by extracting it with a light gas oil at 195° F. According to Selskii,<sup>14</sup> separation of paraffin wax from clay with hot water is exceedingly difficult or even impossible due to the emulsifying properties of the clay.

Weir<sup>15</sup> decolorizes the oil first by heating it with an adsorbent and then cooling the mixture below the crystallization temperature of the wax before filtering. Weir<sup>16</sup> also claims that clay used for color treatment of various stocks is satisfactory for dewaxing purposes and that the clay used in dewaxing can be regenerated repeatedly for this purpose without loss in efficiency.

The plant throughput is generally controlled by the following factors:

1. Viscosity of solution, which has been already discussed.
2. Character of crystallized wax, the effect of which may be controlled to a certain extent by the rate of chilling or, preferably, by increasing the quantity of filter-aid used and by lowering the viscosity of solution.
3. Character of filter-aid.
4. Condition of filter cloth.
5. Mechanical operation of the filter.
6. Ratio of filter-aid to wax recovered, though the use of excessive quantities of filter-aid may result in decreased yields of oil due to soaking. The optimum quantity of filter-aid should, therefore, be determined experimentally for individual stocks.

The use of the Weir process as such for dewaxing purposes is now apparently on a decline, but the use of filter-aids for improving filtering rates in connection with solvents other than naphtha may find some application in the future.

Substances which have been recommended for addition to the oil or oil-solutions before cooling and which crystallize from the oil on chilling before the wax begins to separate out include naphthalene, anthracene,

\* Mitchell-Roberts<sup>11</sup> adds filter-aid before the solution is chilled.

phenanthrene, para-dichlorobenzene, para-dibromobenzene,\* diphenyl,<sup>21</sup> soaps, such as aluminum stearate,<sup>22</sup> colloidal substances of the type of bitumen or grahamite,<sup>23</sup> highly polymerized or condensed high molecular weight paraffins and their halogen, oxygen or sulfur derivatives,<sup>24</sup> phenol,† etc. Some of these substances like naphthalene or phenol are apparently of value primarily for improving the rigidity of the filter cake, while others of the colloidal type seem to influence the wax structure as discussed further below in connection with the pour point inhibitors. In addition to the above improvements in the dewaxing qualities of oils the presence of some of these substances such as phenol in the wax cake may have a beneficial influence on the sweating qualities of the wax produced.<sup>26</sup>

Reagents used for sludging the oil before dewaxing in order to improve its dewaxing characteristics include small quantities of sulfuric acid<sup>27</sup> or other reagents capable of reacting with the oil. This treatment is usually applied to the oil diluted with naphtha or other solvents,<sup>28</sup> and the resulting mixture is chilled and the wax separated by filtering or centrifuging.<sup>29</sup> The so-called "Russian" method of dewaxing oils employed by a few plants in Europe is a development of this idea, but the commercial operation of the plants employing this process shows that the method is well below average expectations even from a mediocre dewaxing process.

Claims have also been made that the dewaxing of oils can be accomplished by heating and shaking them with aqueous solutions of calcium, magnesium, sodium, or zinc chlorides, glycerol, or alcohol, followed by cooling and centrifuging,<sup>30</sup> but the validity of these claims does not seem to have been definitely established yet.

### Electrical Precipitation Methods

In the course of the last few years some of the large oil companies have been conducting experimental studies with the view of substituting the present filtering or centrifugal methods of separating wax from the oil by the electrical precipitation methods similar to those employed for separating water from oil emulsions, elimination of solid particles from gases, etc. A series of patents has been issued covering this development and various structural details of the equipment,<sup>31</sup> but up to the present time this method of separating wax from oil is still in the experimental stage.

\* Deutsche Gasolin A.-G.;<sup>17</sup> Pfaff, Böttger, and Sieweke;<sup>18</sup> Deutsche Gasolin A.-G.<sup>19</sup> Katz<sup>29</sup> claims that the crystallization of wax in presence of naphthalene proceeds very satisfactorily and that the resulting wax cake is easily filtered out from the oil.

† Burk<sup>26</sup> uses for this purpose from 5% to 25% phenol. See also Fussteig.<sup>20</sup>

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## Chapter V

### Solvent Dewaxing

The rapid growth of chemical industries in the course of the last few years and the development of new processes for manufacturing different types of chemicals have supplied the market with a variety of relatively cheap solvents which are superior to naphtha when applied to the dewaxing of petroleum products. The industrial application of these new commercial solvents by the petroleum industry was further rendered feasible by the recent engineering developments which insure continuous plant operation at a minimum loss in handling such solvents at the refinery.

Two methods are apparent which can be applied for separating oil from wax by means of solvents, namely, the wax can be separated as a solid by crystallizing it from the oil solution at low temperatures and as a liquid by employing the selective solvent methods described in connection with solvent refining, provided a solvent is available which is capable of differentiating between the hydrocarbons of high and low melting points on the basis of preferential selectivity at temperatures above the melting point of the wax. The present solvent dewaxing methods employ the first of these principles, but a few isolated laboratory attempts to obtain the desired separation of oil and wax in the liquid phase are also recorded.<sup>1</sup> If such attempts are successful the cost of dewaxing petroleum oils will be greatly reduced due to possibility of eliminating expensive refrigeration and filtering or centrifuge operations which are indispensable with the present type of processes. Further discussion in this chapter is confined, however, only to processes in which wax is removed from the oil solution as a solid phase because these processes alone have, as yet, a practical significance.

#### Ideal Dewaxing Solvent

An ideal solvent for separating the wax from oil by crystallization should possess the following properties:<sup>2</sup>

1. The solvent must be completely miscible with the oil at filtering or centrifuging temperatures and yet must not dissolve the wax crystals at temperatures which can be easily obtained in commercial practice.
2. At temperatures not excessively elevated above those necessary for the complete separation of wax, the solvent should possess a solu-

bility sufficiently high to dissolve all of the wax so as to insure a uniform solution and a proper distribution of solvent and oil.

3. The solvent must be recoverable from both components and easily separated from water. As separation is usually effected by distillation, the boiling point of the solvent must be sufficiently low in order to permit easy removal of the solvent without danger of contaminating it with the low boiling oil fractions.

4. The solvent must be capable of separating the wax in such a form that it can be easily removed from the oil by mechanical means.

5. The solvent must have no chemical action on either oil or wax.

6. The solvent should not introduce complications in the design of the plant equipment by requiring expensive materials to withstand corrosion or high pressures. The solvent should also present no excessive hazards due to its poisonous or inflammable nature.

Several very interesting articles on the poisonous character of commercial solvents employed in petroleum refining, have been published by Francis, covering Benzene,<sup>2a</sup> Phenol,<sup>2b</sup> Chlorex,<sup>2c</sup> Cresol,<sup>2d</sup> Nitrobenzene,<sup>2e</sup> Furfural,<sup>2f</sup> Sulfur Dioxide,<sup>2g</sup> Aniline,<sup>2h</sup> Ketones,<sup>2i</sup> Aldehydes,<sup>2j</sup> and Trichloroethylene.<sup>2k</sup>

7. The cost of the solvent should be low.

8. The thermodynamic properties of the solvent, such as its latent heat of vaporization and specific heat, should be satisfactory in order to avoid excessive refrigeration and distillation costs.

### Practical Dewaxing Solvents

The practical solvents which are now being used commercially do not necessarily answer all of the above requirements though they are usually sufficiently close to them to make these solvents attractive. Moreover, certain undesirable characteristics of solvents can frequently be overcome by proper plant construction without an undue increase in the cost of the equipment.

The use of solvents other than naphtha for dewaxing purposes results in a reduced differential between the pour point of the oil and the chilling temperature. In certain instances even negative differentials are observed, *i.e.*, the pour point of the dewaxed oil is lower than the chilling temperature. For instance, by extracting a Pennsylvania oil with a mixture of 40% methylene chloride and 60% acetone at  $-13^{\circ}\text{F}$ , the pour point of the recovered oil was  $-25^{\circ}\text{F}$ .<sup>3</sup> Such negative differentials, however, are practically never encountered in present commercial practice although it appears feasible that with further developments of solvent dewaxing methods they may not be uncommon.

As already mentioned, a good solvent should completely dissolve the oil at temperatures at which wax crystallizes out. As all solvents dissolve at least minute quantities of wax under all experimental conditions it is evident that the use of excessive quantities of solvents, beyond a

certain optimum, results in a higher pour test of the recovered oil because the quantity of the wax left in the oil after distilling the solvent is directly proportional to the volume of the solvent used. However, due to the negligible solubility of wax in most of the commercial solvents at the extraction temperatures, the above considerations are usually of little commercial importance. This is so because the effect of increasing the quantity of solvent on the pour point of the oil becomes detectable only with solvent ratios considerably above those, which are economical at the plant. The use of very small quantities of solvents may also result, however, in an increase in the pour test because the solubility of wax in oil may be greater than after addition of the solvent, notwithstanding the increase in the total volume of the liquid phase. The above considerations are illustrated by the experimental data presented in Figure 1

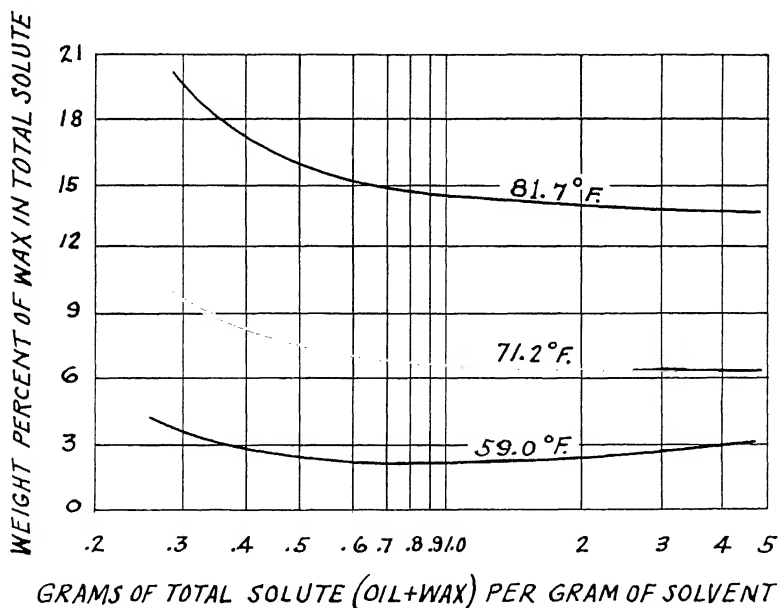


FIGURE 1.—Effects of Hydrocarbon-Pentanol Ratio on Percentage of Wax in Dewaxed Lubricating Oil.

which show the solubility of 122° F. melting point wax in Pentanol,\* and oil mixtures, the quantity of oil used being constant.<sup>4</sup>

A considerable amount of highly interesting work on the relative solubilities of paraffin waxes and lubricating oils in a large variety of

\* A trade name for an isomeric mixture of amyl alcohols synthesized from the pentane fraction of natural gasoline by chlorination and hydrolysis.

solvents has been carried out by Poole and his collaborators during the last few years.<sup>5</sup>

Solubility of wax in acetone and nitrobenzene was determined by Henderson and Ferris,<sup>6</sup> and that of wax and lubricating oils in acetone by Wyant and Marsh.<sup>7</sup> Velikovskii and Zuikov<sup>8</sup> give a review of literature on the solubility of waxes in naphtha, ethylene dichloride, iso-propyl alcohol, acetone, methyl-ethyl ketone and white and yellow ketone oils.

Of the solvents they examined they found that butanol, butyl formate, paraldehyde, pentasol, *n*-butyl aldehyde and diethyl carbinol seemed to offer the most promise as commercial dewaxing solvents. On the basis of their extensive experimental data they recommended the use of the following equation for expressing the solubility of wax in any solvent with respect to temperature:

$$\log W = A (\log T - K)$$

where  $W$  is the solubility of wax in grams per 100 grams of solvent,  $T$  = the absolute temperature in °K (°C + 273),  $A$  = constant dependent on the nature of wax, and  $K$  = constant dependent on the nature of the solvent. The above equation shows that the plot of solubility against the absolute temperature on a logarithmic paper is a straight line. However, the above equation does not give even approximate results when applied to solutions containing oil, though by making certain assumptions the constant  $K$  which characterizes the nature of the solvent with respect to its ability of dissolving wax might be calculated.

The above work although of considerable theoretical interest does not reproduce exactly the conditions encountered in commercial practice, and for this reason, the value of a dewaxing solvent for the refinery should always be determined by investigating the effect of the particular solvent on the lowering of the pour point of actual plant stocks to be dewaxed. This is particularly true due to the existence of a series of compounds intermediate between oil and wax mentioned in Chapter III which are not taken into consideration in the above solubility measurements.

Ba Thi, Strang, Hunter, and Nash<sup>9</sup> discuss principles of solvent dewaxing and recommend a method for graphical interpretation and yield computation by means of triangular diagrams. However, the use of this method does not seem to produce entirely reliable results, particularly due to the incorrect assumption that the melting point of the wax separated from a given oil fraction depends only on its oil content.

When the oil is dewaxed with single solvents it is frequently found that the solubility characteristics of such solvents with respect to both oil and wax are not necessarily suited for dewaxing purposes. By blending such solvents, however, with another solvent the desired balance may be obtained so that the resulting mixture has the required characteristics of a good dewaxing solvent. Thus acetone and methyl-ethyl ketone dissolve practically no wax but at the same time they are unable to dissolve any appreciable quantities of oil, especially at the low temperatures

required in dewaxing. Benzol and toluol, however, are capable of dissolving large quantities of oil with which they are miscible in all proportions, though they likewise dissolve appreciable quantities of the wax. By mixing two such types of solvents in proper proportions a blend can be obtained which has low solvent power for the wax and large solvent power towards the oil under the temperature conditions required for dewaxing. Similar relationships are found among a variety of other solvents such as ethylene dichloride and chloroform, or ethylene dichloride and benzol, furfural and benzol, etc. It is, therefore, possible to obtain the desired solubility characteristics from a dewaxing solvent either by

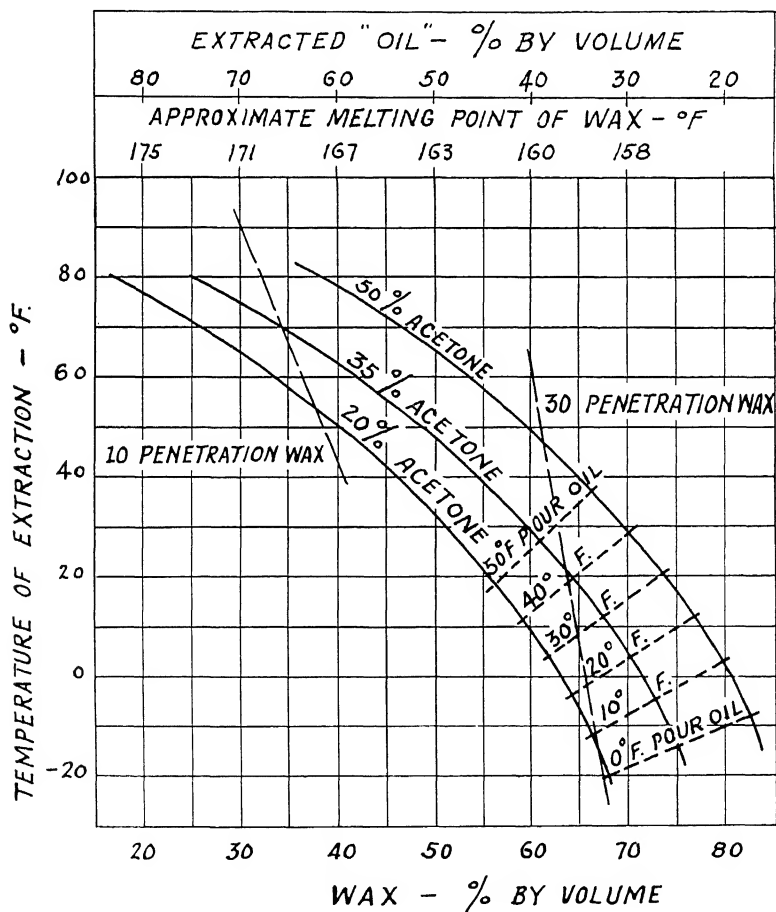


FIGURE 2.—Separation of Oil and Wax from Mid-Century Petroleum by Benzol-Acetone Mixtures.

employing a single solvent, such as trichloroethylene, which has the required properties due to its properly adjusted molecular structure or by employing a mixture of two solvents in which the solubility properties are balanced by adjusting the relative quantities of the two or more solvents having molecules of somewhat dissimilar solubility characteristics. The second method should be considered as being a more flexible one as necessary adjustments can be easily made when such are required in refinery practice.

From the practical viewpoint the best dewaxing solvent is the one which is capable of yielding a maximum quantity of oil of the required pour point for equal operating costs. The possibilities of increasing the yield of oil by properly adjusting the experimental conditions are presented in Figure 2. For better visualization of the existing relationships, petrolatum containing large quantities of oil has been used instead of oil containing relatively small quantities of wax. This petrolatum was obtained from a 150 Saybolt Universal seconds at 210° F. Mid-Continent residuum after treating it with sulfuric acid and dewaxing by naphtha centrifuging. The curves show that the yield of a given pour point oil varies with the relative proportions of acetone and benzol in the dewaxing mixture and the extraction temperature. The same variables have also a corresponding effect on the melting point and penetration characteristics of the separated wax. The yields of oil of a given pour point increase by decreasing the acetone to the benzol ratio employed and lowering the extraction temperature. This at the same time results in lower yield of wax but of improved melting point and penetration characteristics. The separation between the oil and the wax is, therefore, sharper when the oil is separated at low temperatures by employing solvent mixtures rich in benzol. In carrying out such quantitative extractions it will also be noted that the viscosity of oils of equal pour point separated from the wax is lower for the lower oil yields, which indicates that the oil retained by the wax is of higher viscosity than the recovered oil. This indicates that the oil is separated from the wax in a somewhat selective manner. This can be expected, however, as acetone as well as ethylene dichloride and a variety of other dewaxing solvents have more or less distinct preferential solubility characteristics towards the oil constituents.

### **Separation of Water From Solvents**

Some of the solvents have the tendency to dissolve more or less large quantities of water which interferes with the dewaxing operations by decreasing the solubility of oil in the solvent and by deposition of solid ice in the transfer lines. This problem becomes of particular importance when solvents are removed from oil by steam distillation. Although under certain conditions the presence of water may be desirable, as mentioned in the previous chapter, in general, however, its presence should be avoided at least above a certain optimum limit. This is generally true

for all solvents employed in oil refining and for this reason the discussion below is not restricted to dewaxing solvents alone.

In general, solvents can be divided into those which do form, and those which do not form, constant boiling mixtures with water, while in respect to their solubility characteristics they may be immiscible, partially miscible or completely miscible with the water. The table below presents these characteristics of commercial solvents.\*

TABLE 6—Properties of Commercial Solvents

| Solvent              | Boiling<br>Point<br>Deg. F. | Solubilities at 100° F.      |                              | Constant<br>Boiling<br>Mixture,<br>Boiling<br>Point<br>Deg. F. | Composition<br>Constant<br>Boiling<br>Mixture<br>Overhead<br>Wt. %<br>Solvent |
|----------------------|-----------------------------|------------------------------|------------------------------|--|---|
|                      |                             | Solvent<br>in Water<br>Wt. % | Water<br>in Solvent<br>Wt. % |  |   |
| Acetone              | 133                         | ∞                            | ∞                            | none   | none  |
| Aniline              | 364                         | 3.8                          | 5.6                          | 209  | 23.1  |
| Benzol               | 176                         | 0.16                         | 0.11                         | none   | none  |
| Carbon tetrachloride | 170                         | 0.09                         | 0.01                         | none   | none  |
| Chlorex              | 353                         | 1.2                          | 1.1                          | 204-207  | ....  |
| <i>o</i> -Cresol     | 375                         | 3.0                          | 14.5                         | 210  | 6   |
| <i>m</i> -Cresol     | 396                         | 2.5                          | 14.5                         | 210  | 6   |
| <i>p</i> -Cresol     | 396                         | 2.2                          | 16.5                         | 210  | 6   |
| Ethylene dichloride  | 182                         | 0.9                          | ....                         | 158  | 91.8  |
| Furfural             | 323                         | 9.0                          | 6.5                          | 208  | 35  |
| Methyl ethyl ketone  | 175                         | 19.0                         | 10.2                         | 164  | 88.6  |
| Nitrobenzene         | 412                         | 0.3                          | 0.35                         | 211  | 15.3<br>(14)  |
| Phenol               | 358                         | 9.4                          | 32.5                         | 210  | 9   |
| Propane              | — 48                        | ....                         | ....                         | none   | none  |
| Sulfur dioxide       | 14                          | ....                         | ....                         | none   | none  |
| Toluol               | 231                         | 0.05                         | ....                         | none   | none  |
| Trichloroethylene    | 188                         | 0.16                         | 0.05                         | 167  | ....  |

Whenever a solvent does not form constant boiling mixtures and the differential between the boiling point of the solvent and that of the water is reasonable, separation can be accomplished by fractional distillation provided corrosion difficulties, such as are encountered in sulfur dioxide-water mixtures, are not beyond the usual tolerances of the present commercial equipment. In tertiary mixtures, such as benzol-acetone-water, complications may arise due to the solubility of one of the components, acetone, in the two other components, water and benzol, which are mutually insoluble. The presence of acetone in water, however, results in the solubility of benzol in such mixtures. This difficulty can be avoided by keeping the concentration of one of the components, acetone, in water below the point where any appreciable solubility of the other component, benzol, in the water phase would result.†

\* Smoley and Kraft<sup>10, 11</sup> give a very interesting discussion on this subject to which the readers are referred for further details.

† Myers<sup>12</sup> describes methods which are applicable for separating water from acetone-benzol mixtures.

Solvents forming constant boiling point mixtures with water but having relatively small mutual solubilities, such as ethylene dichloride, trichloroethylene, chlorex or nitrobenzene, can be recovered to a large extent free from water. The small portion of the solvent forming the constant boiling mixture is passed into a separator from which the solvent phase, saturated with water, is added directly to the dry solvent, since the total quantity of water thus introduced into the dry solvent is usually insufficient to have an adverse effect on its characteristics. The water phase from the separator is then distilled in order to obtain free water and the constant boiling mixture of water and solvent, the latter being handled in the way above described.

Solvents forming constant boiling mixtures and having appreciable mutual solubilities in water are handled in a variety of ways, depending on the nature of the mixtures, which can be classified as follows:

Solvent-water mixtures which show a considerable difference in composition between that of the constant boiling point mixture and that of the solvent phase of the cooled condensate may be separated by distilling the two phases separately. This results in separating the solvent from the constant boiling point mixture in one still and water from the constant boiling point mixture in another still. The two phases obtained on liquefaction of the constant boiling point mixtures in either still are then redistilled in the respective stills, in order to obtain further separation.<sup>13</sup> This method is applicable to separating mixtures of water with furfural or with alcohols, etc. For mixtures where the difference in the composition of the constant boiling point mixture and the condensate is small, such as mixtures of water with cresol, phenol, or aniline, the saturated water phase may be converted into steam which is then introduced at the bottom of the fractionating tower.<sup>14</sup>

It appears feasible also to add to the constant boiling mixture a third component which is capable of forming a constant boiling mixture with water at the expense of the water present in the original constant boiling mixture. This may be accomplished by simply supplying the third component as reflux at the top of the fractionating column.<sup>15</sup>

It is likewise possible to separate the constant boiling point mixtures by saturating them with salts such as sodium chloride or sodium sulfate which resolve the solutions into two phases by "salting out" the solvent, by dissolving the solvent from water through use of another solvent which is immiscible with water but which dissolves the other component of the constant boiling mixture, etc. The commercial application of the above methods depends on the individual problems encountered in refinery practice which must, therefore, be studied separately.

## Commercial Solvent Dewaxing Processes

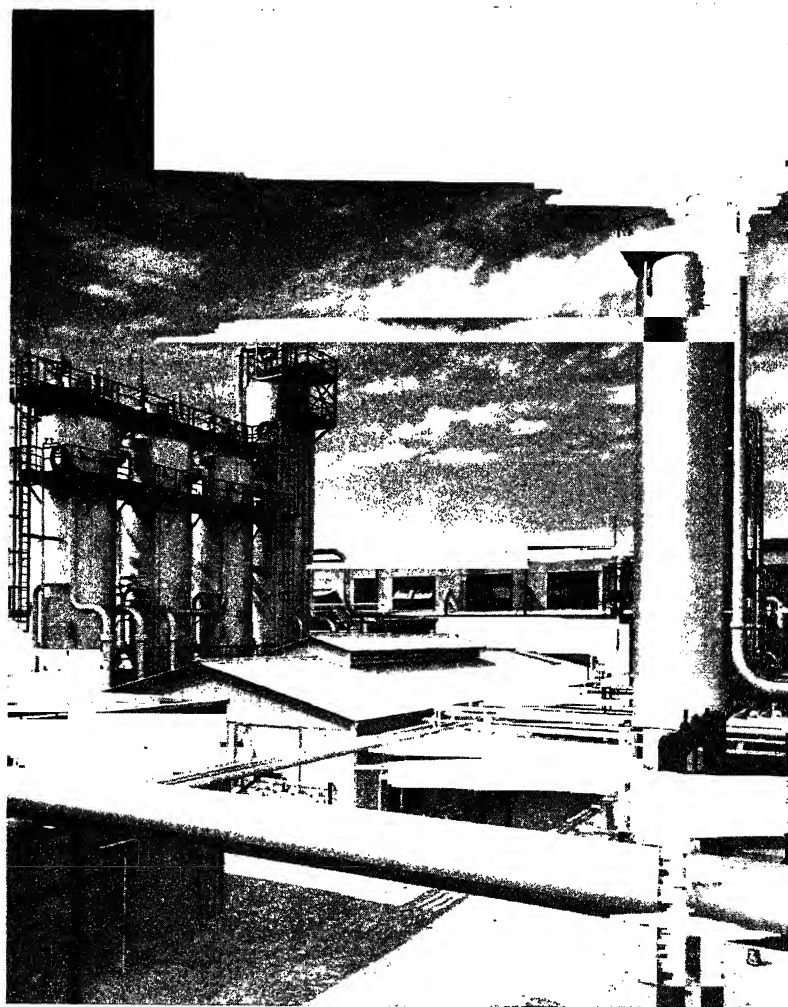
Solvents differ in their effect on the physical properties of the wax phase obtained on cooling. With some solvents the separated wax can be easily removed by filtration while with other solvents this separation must be accomplished by centrifuging. The choice of solvent, therefore, depends on the refinery system employed for effecting this separation, and when mixtures of solvents are used the relative proportions of the two solvents are sometimes governed by this consideration. For instance, in Figure 2, which shows the effect of various benzol-acetone mixtures on the yield and properties of the products obtained in extracting commercial petrolatum, the solvent mixtures containing less than 20% acetone could not be filtered, while those containing 35% acetone or more were in this respect very satisfactory. As already mentioned, the use of large quantities of acetone resulted in high dewaxing losses. For this reason, the optimum quantity of acetone would be limited on the lower concentrations by the filterability of the wax cake and on the upper side by the excessive oil losses.

The solvent must be, evidently, inert towards the oil or wax under the conditions employed in the dewaxing operations. Some solvents, particularly those containing chlorine or some unstable chemical radicals of the aldehyde or similar types, may introduce certain difficulties in plant operations. These difficulties are usually solved, however, by employing proper temperature ranges in distilling off the solvent under vacuum, etc., although they cannot be overlooked in choosing the dewaxing solvent for plant use.

The present commercial solvent dewaxing processes employ propane, benzol-acetone mixtures, and chlorinated hydrocarbons, although a variety of other organic solvents has been proposed for the same purpose which may find practical application. These processes are described below.

### *Propane Dewaxing Process*

As already mentioned, the use of naphtha in conventional dewaxing methods is open to a variety of objections which need not be repeated here. As one of these objections is the high solubility of wax in naphtha at temperatures at which the wax is separated from the oil, investigations were made in order to determine whether this solubility varies with the grade of naphtha employed. The work of Sachanen<sup>16</sup> showed that the solubility of paraffins increases with the decrease of their melting point and with the decrease in the molecular weight (or specific gravity or boiling point) of the naphtha used. This is well illustrated by the following experimental data of Weber and Dunlap<sup>17</sup> on solubilities of paraffin wax of 132.8° F. (56° C.) melting point, and 0.775 specific gravity at 68° F. (20° C.), in various hydrocarbons.



*Courtesy: M. W. Kellogg Company*

PLATE I.—Propane Dewaxing Unit.

TABLE 7—Solubility of Paraffin Wax

| Temperature |      | Grams per 100 c.c. of Solvent |                  |                   |                  |                    |
|-------------|------|-------------------------------|------------------|-------------------|------------------|--------------------|
| ° F.        | ° C. | <i>n</i> -Pentane             | <i>n</i> -Hexane | <i>n</i> -Heptane | <i>n</i> -Octane | <i>iso</i> -Decane |
| 32          | 0    | ....                          | 2.77             | 1.37              | 0.99             | ....               |
| 41          | 5    | ....                          | 3.69             | 2.18              | 1.69             | 0.94               |
| 50          | 10   | 5.11                          | 4.81             | 3.55              | 2.90             | 1.44               |
| 59          | 15   | 6.94                          | 6.07             | 5.06              | 4.24             | 2.74               |
| 68          | 20   | 9.53                          | 8.31             | 7.18              | 5.93             | 4.98               |
| 77          | 25   | 17.16                         | 16.23            | 14.36             | 11.66            | 9.17               |

The above shows that heavy naphtha is preferable to the light naphtha from the viewpoint of wax solubility relationships, although the use of light naphtha is obviously desirable for effecting the maximum possible

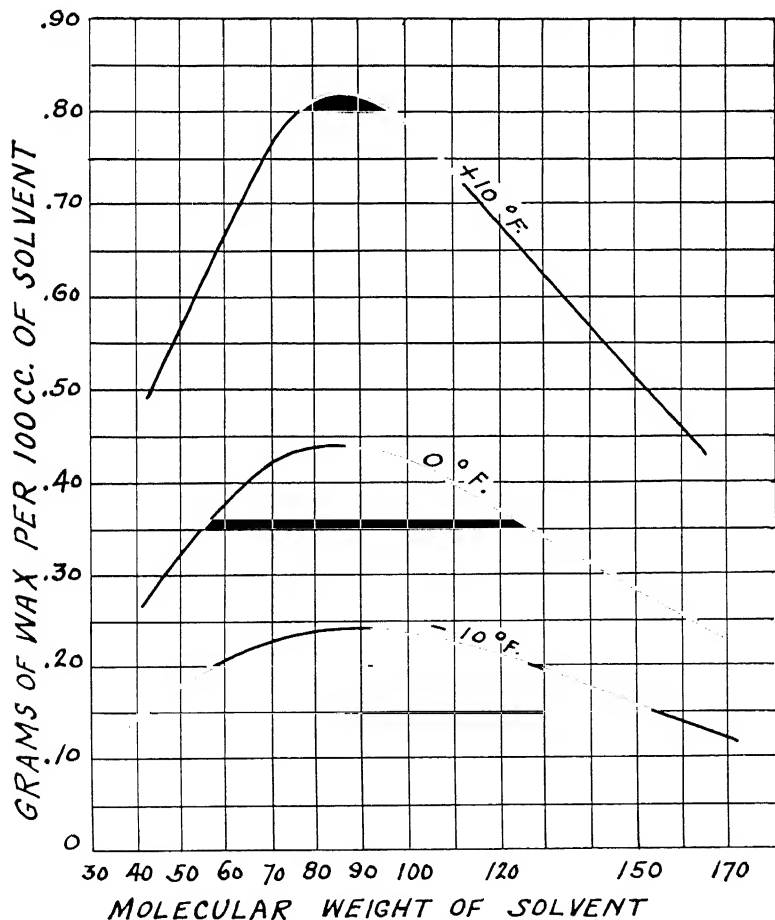


FIGURE 3.—Solubility of 122° F. Melting Point Wax in Hydrocarbon Solvents of Different Molecular Weights.

decrease in viscosity of the oil-naphtha solutions for a given dilution ratio.

Bahlke, Giles, and Adams<sup>18</sup> give the following comparisons of the specific gravities and viscosities of butane and naphtha solutions of an S.A.E. 50 distillate oil at  $-10^{\circ}\text{F}$ .

TABLE 8—Solutions of S.A.E. 50 Distillate Oil

| % Oil | cc Solvent | Specific Gravity |                 | Viscosity (Poises) |                 |
|-------|------------|------------------|-----------------|--------------------|-----------------|
|       |            | Naphtha Solution | Butane Solution | Naphtha Solution   | Butane Solution |
| 15    | 85         | 0.813            | 0.667           | 0.025              | 0.005           |
| 25    | 75         | 0.828            | 0.700           | 0.047              | 0.009           |
| 35    | 65         | 0.841            | 0.733           | 0.101              | 0.018           |

Sage, Sherborne and Lacey<sup>19</sup> give viscosities of methane and propane solutions in crystal oil.

The naphtha employed at the different refineries is usually the one which gives a proper balance between these two opposing tendencies.\*

The above investigations covered, however, only hydrocarbons which are liquid at ordinary temperatures. Further researches of the similar type with liquefied normally gaseous hydrocarbons showed that solubility of wax with the decrease in the molecular weight (or boiling point) of the hydrocarbon solvent reaches a certain maximum after which the solubility begins to decrease, apparently reaching its maximum somewhere between butanes and pentanes, as illustrated by the curves in Figure 3 on solu-

\* Towne<sup>20</sup> patented the use of cracked naphtha for dewaxing purposes.

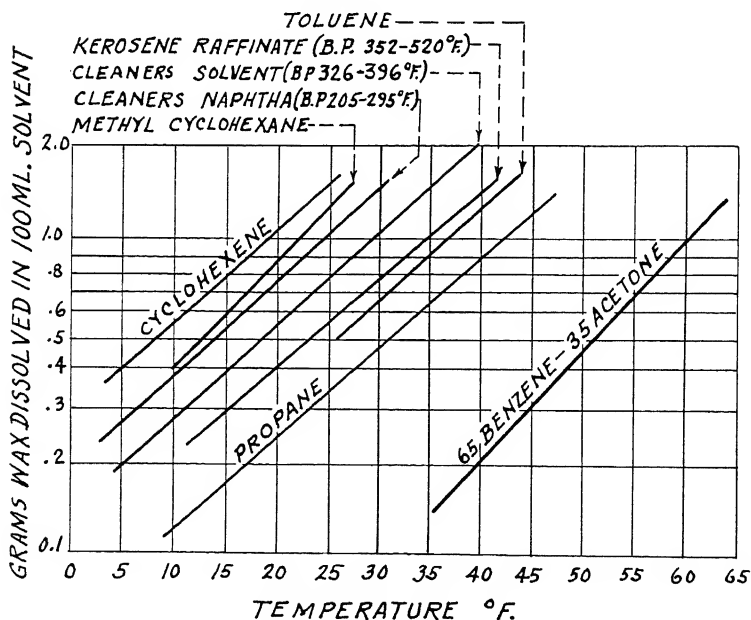


FIGURE 4.—Solubility of  $123^{\circ}\text{F}$ . Melting Point Wax in Various Hydrocarbon Solvents.

bilities of 122° F. melting point wax in hydrocarbon solvents of different molecular weights.<sup>18</sup> Similar comparisons between propane and other dewaxing solvents is also presented in Figure 4 which shows solubilities of 123° F. melting point wax in a variety of solvents at various temperatures.<sup>21</sup> Moreover, these liquefied hydrocarbons offer the possibility of refrigerating the dewaxing mixture by evaporating some of the liquefied hydrocarbon which can be accomplished by mere reduction in pressure. The utilization of this principle is self-evident as by lowering the pressure, a certain quantity of the liquefied gas evaporates until the quantity of heat extracted from the main body of the liquid, to supply the latent heat of vaporization for the vaporized fraction, becomes equal to that required for lowering the remaining portion of the liquid to the temperature corresponding to this reduced pressure. Besides being a dewaxing solvent, propane and related hydrocarbons have also deasphalting properties which are discussed in connection with the deasphalting processes and are not considered here.

Numerous patents were issued covering the use of propane and similar hydrocarbons as dewaxing agents.<sup>22</sup> These patents refer both to the application of liquefied normally gaseous hydrocarbons for dewaxing purposes and to the different mechanical details which are very important

TABLE 9—Physical Properties of Propane

|  |          |
|--|----------|
| Molecular weight   | 44.08    |
| Boiling point at 760 mm. Hg., ° F.                           | - 43.8   |
| At 30 ins. Hg.=14.73 lbs./sq. in., ° F.                      | - 43.7   |
| Vapor pressure at 60° F. lbs. per sq. in., abs.              | 107.2    |
| At 70° F., lbs. per sq. in., abs.                            | 124.2    |
| At 100° F., lbs. per sq. in., abs.                           | 186.8    |
| At 105° F., lbs. per sq. in., abs.                           | 199.1    |
| At 130° F., lbs. per sq. in., abs.                           | 269.6    |
| Critical temperature, ° F.                                   | 212.2    |
| Critical pressure, lbs. per sq. in., abs.                    | 643.3    |
| Critical volume, cu. ft. per lb.                             | 0.06896  |
| Liquid at 60° F. and vapor pressure:                         |          |
| Specific gravity, gr./cc.                                    | 0.5111   |
| Specific gravity (H <sub>2</sub> O=1 at 60° F.)              | 0.5116   |
| A.P.I. gravity   | 145.1    |
| Weight per gallon, lbs.                                      | 4.265    |
| Vapor at 60° F. and 14.73 lbs. abs.:                         |          |
| Compressibility factor                                       | 0.9841   |
| Density, gr./cc.   | 0.001836 |
| Density, lbs./cu. ft.  | 0.1183   |
| Specific volume, cu. ft. per lb.                             | 8.451    |
| Specific gravity (Air=1)                                     | 1.5404   |
| Cu. ft. per gal. of liquid at 60° F.                         | 36.05    |
| Cu. ft. per gal. of liquid at 60° F. (perfect gas)           | 36.63    |
| Latent heat at boiling point, B. t. u./lb.                   | 183.0    |
| At boiling point, B. t. u./gal.                              | 780.0    |
| Specific heat of liquid at 60° F.                            | 0.658    |
| Of vapor at 60° F. and 14.73 lbs. abs. at constant pressure  | 0.404    |
| Ratio of specific heats, C <sub>p</sub> /C <sub>v</sub>      | 1.162    |
| Heating value of liquid, high B. t. u./lb.                   | 21,493   |
| Of liquid, low, B. t. u./lb.                                 | 19,940   |
| Of liquid, high, B. t. u./gal.                               | 91,670   |
| Of liquid, low B. t. u./gal.                                 | 85,050   |
| Of vapor, dry, high, B. t. u./cu. ft.                        | 2,555    |
| Of vapor, dry, low, B. t. u./cu. ft.                         | 2,376    |
| Of vapor, sat. with H <sub>2</sub> O, high, B. t. u./cu. ft. | 2,511    |
| Of vapor, sat. with H <sub>2</sub> O, low, B. t. u./cu. ft.  | 2,335    |
| Limits of inflammability, per cent                           | 2.3-9.5  |

for successful operation of the process on a commercial scale. Many of these patents refer also to the use of propane for both dewaxing and deasphalting purposes.

Pure propane has the physical properties given in Table 9.<sup>23</sup> \*

In commercial practice the oil is blended with two to three volumes of propane at 180-200 lbs. per sq. in. pressure, which is required in order to maintain propane in a liquid state at the mixing temperature of 90-100° F. Sometimes higher mixing temperatures up to 130° F. or more are required with correspondingly higher propane pressures. After a uniform mixture is obtained the pressure is released and the mixture chilled by evaporating part of the propane.† After the desired temperature is reached the solution with the suspended particles of wax is filtered through a discontinuous or continuous type of filter.<sup>26</sup>

The wax cake is washed with cold propane which is then used for diluting the fresh oil charge, and loosened by a blow back of propane gas. With batch filters, the loosened cake drops to a conveyor by gravity, while with continuous filters the cake is deflected to a conveyor blade. At long intervals, filter cloths may be renovated by a hot naphtha wash. Propane is then removed from oil and wax by distillation, the last traces of propane being separated from the oil at atmospheric pressure and with the use of steam. The propane dewaxing process, which is applicable to both distillate and residual oils, is now being used commercially by several large oil companies, notably by the Standard Oil Co. of Indiana, Shell Oil Co., Union Oil Co. of California and Kendall Refining Co.

The usual temperature differential between the chilling temperature and the pour point of the oil is 25-35° F. which is less than in naphtha dewaxing. The rate of chilling the solution is also claimed to be of less importance than with naphtha and may be as high as several degrees Fahrenheit per minute, while with naphtha the rate should not exceed a few degrees per hour. However, a number of different wax structures can be obtained in propane dewaxing and for this reason variables such as mixing temperature, propane-oil ratio, chilling conditions, and the presence of crystallizing agents (such as asphaltic compounds) which affect these structures, cannot be entirely disregarded.‡ In general, shock chilling has an adverse effect on the filterability of the wax cake. Some agitation during the chilling period appears to be beneficial, though

\* For further details see Lacey and Sage,<sup>24</sup> who carried out an extensive investigation of the properties of propane over a wide range of temperature and pressure conditions and developed a series of graphs which are of much importance in designing plant equipment.

† Voorhees<sup>25</sup> uses the same principle of self-refrigeration with other solvents than propane, namely, with alkyl and alkylene ethers which he recommends as dewaxing solvents.

‡ Anderson and Talley<sup>27</sup> present the results of their thorough study on wax precipitation from propane solution, as applied to a residual oil.

violent stirring must be avoided. The propane to oil ratio becomes important only when it is low, the 1.6 to 1 ratio being, apparently, the lower limit for a good wax structure when dealing with residual stocks. Lower ratios give gel formations which are difficult to transport and impossible to filter. The presence of small quantities of asphaltic matter or similar substances appears to be of assistance in improving filtering rates as these substances seem to act as filter-aids or as cementing materials for agglomeration of the wax crystals. The plant filter rates are frequently about 3.5-4.0 gallons of dewaxed oil per square foot of filtering area per hour, although by taking necessary precautions apparently they can be improved still further. The commercial wax cake usually contains about 30% oil, which cannot be considered as being high.

Hodus<sup>28</sup> gives a method for estimating oil losses in petrolatum from centrifuging operations which is, however, applicable also to filtering processes. The method is based upon the assumption that petrolatum contains oil similar to the one obtained after dewaxing and that the oil is in solution with all of the naphtha (or solvent) which is present in the dilute petrolatum. By knowing the naphtha (or solvent) content of the wax cake and the oil to the naphtha (or solvent) ratio in the dewaxed solution, the quantity of oil present in the wax cake can be estimated by simple arithmetical calculations.

### *Benzol-Acetone Dewaxing Process*

This process, also known as the ketone-benzol process, has been developed by the Texas Oil Co. and as other dewaxing processes can be employed both for the removal of wax from the oil,<sup>29</sup> and for removing oil from the wax.<sup>30</sup> Acetone is used due to its selective solubility characteristics toward the wax and oil constituents and its ability to precipitate the wax in well defined and easily filterable crystals, while benzol is added to the mixture in order to supply the required solvent power in which acetone is deficient. In adjusting the proper benzol-acetone blends the following factors, which were to a certain extent discussed in the beginning of this chapter, should be taken into consideration:

1. For a given pour test the temperature to which the mixture must be chilled is lower for blends containing larger proportions of benzol.
2. For the maximum yield of the dewaxed oil of a given pour test the proportion of benzol should be high (and the chilling temperature low).
3. For improving filtering rates the proportion of acetone in the blend should be high.

Although the process is usually referred to as the benzol-acetone process, other solvents are frequently employed as partial or complete substitutes for benzol and acetone. Of these substitutes toluol and methyl-ethyl ketone are of considerable commercial importance. Toluol is used interchangeably with benzol when low chilling temperatures are employed because if benzol is used alone it may crystallize out of the

solution due to its high melting point. Toluol is also more effective than benzol in lowering the miscibility temperature of oil—solvent mixtures and preventing separation of valuable high viscosity index constituents with the solidified wax.\* Methyl-ethyl ketone is somewhat cheaper and has slightly better solubility characteristics than acetone which justifies its use at the plant, although it is frequently necessary to employ it in somewhat larger quantities than acetone in order to obtain similar results. These differences are insufficient, however, to warrant a separate discussion of these solvent substitutes. Besides methyl-ethyl ketone other ketones were also recommended as substitutes for acetone, while solvents similar in their solubility characteristics to benzol or toluol were likewise suggested.

Govers<sup>32</sup> specifies a mixture of acetone, methyl-ethyl ketone, benzol and toluol; Wagner<sup>33</sup> substitutes methyl-ethyl ketone for acetone; Gross and Oberbaugh,<sup>34</sup> and Texaco Development Corp.,<sup>37</sup> use methyl-iso-butyl ketone blended or not blended with gasoline, benzol, propane, butane and other similar solvents; Kellogg<sup>38</sup> employs a blend of acetone and solvent kerosene extract rich in aromatic compounds; McCarty and Skelton<sup>39</sup> use a mixture of propane, ortho-dichlorobenzene and acetone or methyl-ethyl ketone; van der Waerden<sup>40</sup> and N. V. de Bataafsche Petroleum Maatschappij,<sup>41</sup> dewax with acetone or methyl-ethyl ketone and tetrahydronaphthalene; Texaco Development Corp.<sup>42</sup> uses cyclic ketones containing from four to seven carbon atoms, particularly cyclohexanone, in presence or absence of diluents such as propane or benzol; Pevere<sup>43</sup> specifies cyclohexanone; Knowles<sup>45</sup> employs a mixture of ketones; Govers<sup>46</sup> utilizes methyl-ethyl ketone and toluene, xylene or cumene.

The following table summarizes the most important properties of acetone, methyl-ethyl ketone, benzol and toluol.

TABLE 10—Properties of Solvents

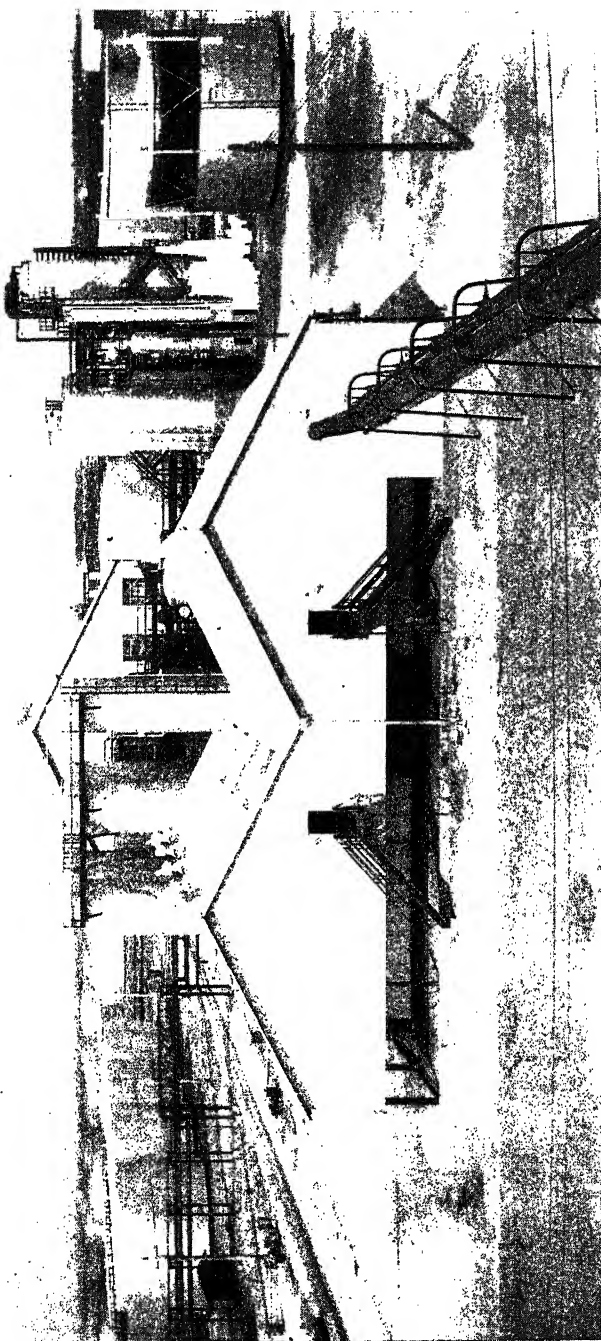
|   | Acetone | Methyl-Ethyl<br>Ketone | Benzol | Toluol |
|---|---------|------------------------|--------|--------|
| Molecular weight                          | 58.05   | 72.06                  | 78.05  | 92.06  |
| Boiling point, ° F.                       | 133.0   | 175.3                  | 175.3  | 230.9  |
| Melting point, ° F.                       | -137.7  | -123.5                 | 41.9   | -139.2 |
| Specific gravity at 68° F.                | 0.7915  | 0.8050                 | 0.878  | 0.866  |
| Viscosity at 77° F., centipoises          | 0.316   | 0.401                  | 0.647  | 0.586  |
| Vapor pressure at 68° F. mm. Hg.          | 184.8   | 77.5                   | 76.0   | 22.0   |
| Flash point (closed cup), ° F.            | 2       | 19                     | 10     | ....   |
| Specific heat, B. t. u./lb./° F.          | 0.527   | 0.550                  | 0.410  | 0.398  |
| Latent heat of vaporization, B. t. u./lb. | 225.0   | 190.8                  | 169.7  | 155.7  |
| Refractive index at 68° F.                | 1.3591  | 1.3791                 | 1.5014 | 1.4962 |

In commercial practice mixtures containing about 25-40% acetone or methyl-ethyl ketone, 12-25% toluol, and 40-60% benzol are employed.<sup>47</sup>

In the oil-acetone-benzol blends commonly used in dewaxing, benzol usually remains in solution at temperatures above 0° F., although its melting point is 41.9° F.

The oil is diluted with 3 to 4 volumes of such mixture and chilled to about 5° F. below the desired pour point of the oil. Larger differentials between the pour point of the oil and the chilling temperature may some-

\* Hall and McCarty<sup>21</sup> discuss miscibility relations in solvent dewaxing.



*Courtesy: Texaco Development Corporation*

PLATE II.—Benzol-Ketone Solvent Dewaxing Unit.

times be required, however, in dewaxing oils of rather unusual characteristics or when the maximum oil recovery is of primary economic consideration. The mixture of solvent and oil is chilled rapidly at a rate which may be as high as 90-100° F. in 1 to 3 hours. These rapid chilling rates do not appear to be objectionable with respect to the filtering rates. The cooled solution is filtered and solvents recovered by distillation. Pressure or vacuum filters are used, the vacuum filters being advantageous by permitting continuous plant operation. The procedure is substantially the same for distillate or residual stocks. The wax cake is washed with cold solvent for removing the oil and this wash solvent is then employed for diluting the fresh portion of the oil charge.

Pretreatment of stocks to be dewaxed with clay or sulfuric acid and clay, which is customary in naphtha dewaxing, is not required. Some difficulties may be encountered only in dewaxing highly treated oils containing small quantities of low melting point waxes, but these conditions are seldom, if ever, encountered in commercial practice. In preparing the initial solvent-oil blend it is likewise frequently possible to avoid the use of high mixing temperatures in order to obtain a homogeneous solution, although this is often desirable with high viscosity or residual stocks in order to improve filtering rates and yields of the dewaxed oil. With such type of stocks heating to temperatures 50-60° F. above the complete solution temperatures may be of importance.

The benzol-acetone process is now being used by a number of large petroleum companies which include the Texas Oil Co., Socony-Vacuum Oil Co., Inc., Atlantic Refining Co., Gulf Refining Co., etc.

### *Dewaxing with Chlorinated Solvents*

A variety of chlorinated hydrocarbons were proposed for dewaxing petroleum oils as well as their mixtures or mixtures with other types of substances.

Tanne and Oberländer<sup>48</sup> use a halogen substitution product of unsaturated hydrocarbon such as acetylene dichloride; Tanne and Oberländer<sup>49, 50, 51</sup> specify carbon tetrachloride which is also discussed by Lederer and Beattie,<sup>52</sup> Backlund,<sup>53</sup> Aktiebolaget Separator-Nobel,<sup>54, 55</sup> Bergedorfer Eisenwerk A.-G.,<sup>56, 57, 58</sup> cover the use of chloroform, carbon tetrachloride, or a similar liquid of specific gravity greater than that of the heaviest wax which may be precipitated. Carlisle and Levine,<sup>59</sup> and Carlisle,<sup>60, 61</sup> specify and discuss the use of methylene dichloride. Edeleanu Ges.<sup>62, 63</sup> recommends a halogen substituted hydrocarbon which is gaseous at ordinary temperatures and belongs to the acyclic series, *e.g.*, methyl chloride, ethyl chloride or dichlorodifluoromethane; Jones<sup>64</sup> uses dichloroethane; Atwell<sup>65</sup> specifies the use of a normally gaseous fluoride of a hydrocarbon containing not more than two carbon atoms such as methyl or ethyl fluorides and which does not contain more than two chlorine atoms; Ramser<sup>66</sup> employs methyl chloride, ethyl chloride or dichlorodifluoromethane under pressure; Sharples Specialty Co.,<sup>67</sup> and Jones,<sup>68, 69</sup> use 1,3-dichloro-2-methylpropane; Standard Oil Development Co.<sup>70</sup> employs carbon tetrachloride, ethylene dichloride or similar chlorinated hydrocarbons; Standard Oil Development Co.<sup>71</sup> uses a mixture of two types of chlorinated solvents such as ethylene dichloride and chloroform or the corresponding derivatives of bromine and fluorine; Jones<sup>72, 73</sup> dewaxes oils with a chlorinated hydrocarbon, such as ethylene, methylene or propylene dichlorides diluted with

benzol, naphtha or similar solvents; McCarty and Skelton<sup>74</sup> use a dewaxing solvent composed of *o*-dichlorobenzene, an alkyl ether of ethylene and diethylene glycol; McCarty and Skelton<sup>75</sup> recommend a blend of *o*-dichlorobenzene and amyl alcohol; Voorhees,<sup>76</sup> and Livingstone,<sup>77, 78</sup> specify mixtures of two solvents one of which is a poor wax solvent such as ethylene dichloride, and the other a good wax solvent such as benzol; McCarty and Skelton<sup>79</sup> use ethylene dichloride and amyl alcohols; Tanne and Oberländer<sup>80</sup> employ chloroform or carbon tetrachloride to which acetic or similar acids might be added; McCarty and Skelton<sup>81</sup> employ orthodichlorobenzene and ethylene dichloride; McCarty and Skelton<sup>82</sup> specify a blend of 60% amylene dichloride and 40% methyl-ethyl-ketone; McCarty and Skelton<sup>83</sup> use isopropyl ether and ethylene or propylene dichloride; McCarty and Skelton<sup>84</sup> specify propylene dichloride and ethylene glycol ethyl ether; I. G. Farbenindustrie A.-G.<sup>85</sup> uses mixtures of a chlorinated hydrocarbon such as carbon tetrachloride, with methyl-ethyl ketone or alcohols such as butyl alcohol or a mixture of methyl-ethyl ketone with alcohols; Bray<sup>86</sup> employs propane with di- or tri-chloroethylene; Sharples Specialty Co.<sup>87</sup> employs ethylene dichloride and benzol; Standard Oil Development Co.<sup>88</sup> dewaxes with carbon tetrachloride, ethylene dichloride, bromoform, chlorobenzol or with a mixture of dichloroethylene and benzol or dichloropropane, toluol and xylol; Aktiebolaget Separator-Nobel<sup>89</sup> employs ethylene chloride and acetone; Jones<sup>90</sup> uses dichloroethane and a properly selected petroleum fraction; N. V. de Bataafsche Petroleum Maatschappij<sup>91</sup> uses chloro- or bromohydrocarbon derivatives; Sharples Specialties Co.<sup>92</sup> recommends trichloroethane; Govers<sup>93</sup> dewaxes with a mixture of ethylene dichloride and a polar substance, such as liquid sulfur dioxide, acetone or methyl-ethyl ketone; Wiles<sup>94</sup> uses ethylene dichloride.

The use of such mixtures is frequently desirable for the same reasons as those explained in connection with the benzol-acetone process.

Although chlorinated hydrocarbons may be employed in connection with both filtering or centrifuging methods for separating the wax, they are practically always employed in connection with the centrifuge methods for which they are particularly adapted due to the high specific gravity of the solvent. For improving the yield of the dewaxed oil double centrifuging is sometimes employed.<sup>95</sup>

Centrifuges which are used in connection with the chlorinated solvents are of a different type than those commonly used in naphtha dewaxing as wax separates out at the bowl of the centrifuge and not on the outside of the revolving cylinder. Scrapers are frequently employed for the removal of crystalline wax when such wax is present in sufficient quantities to interfere with the smooth discharge of the separated wax. Such centrifuges are, therefore, suitable for removing wax from both residual and distillate stocks.

In general, the chlorinated solvents have a tendency toward liberating chlorine (or hydrochloric acid) on heating, which results in darkening of the oil when the solvent is removed by distillation, and in the corrosion of the refinery equipment. For this reason special care should be exercised in selecting the proper chlorinated solvent of sufficient chemical stability and in employing low distillation temperatures at which the decomposition of the solvent is negligible. Some of the chlorinated solvents, such as carbon tetrachloride, may be in this respect more objectionable than others as represented by trichloroethylene,<sup>96</sup> or ethylene dichloride, which to a great extent determines their practical application.

Two processes which involve the use of chlorinated hydrocarbons have reached at the present time the commercial state of development: the Separator-Nobel dewaxing process and the Bari-Sol dewaxing process which are described below.

### *Separator-Nobel Dewaxing Process*

The process is also frequently referred to as the S-N dewaxing process or as the trichloroethylene process. It is being used commercially by the Standard Oil Co. of New Jersey.<sup>97</sup> Although other chlorinated solvents can be used in the same type of commercial equipment, trichloroethylene or "tri," having the following physical characteristics, is actually employed at the plant.

TABLE 11—Physical Properties of Trichloroethylene

|   |        |
|---|--------|
| Molecular weight ( $C_2HCl_3$ )                           | 131.4  |
| Specific gravity at 32° F.                                | 1.4996 |
| Specific gravity at 59° F.                                | 1.4762 |
| Specific gravity at 86° F.                                | 1.4514 |
| Specific gravity at 113° F.                               | 1.4262 |
| Specific gravity at 139° F.                               | 1.3937 |
| Boiling point, ° F.                                       | 188    |
| Freezing point, ° F.                                      | —126   |
| Viscosity (centipoises) at 77° F.                         | 0.550  |
| Viscosity (centipoises) at 122° F.                        | 0.446  |
| Viscosity (centipoises) at 167° F.                        | 0.371  |
| Specific heat, B. t. u./lb. ° F.                          | 0.23   |
| Latent heat of vaporization, B. t. u./lb.                 | 104.5  |
| Solubility of water in trichloroethylene, % wt. at 50° F. | 0.017  |
| Solubility of water in trichloroethylene, % wt. at 82° F. | 0.035  |

It is also claimed that trichloroethylene is non-corrosive, does not hydrolyze nor decompose on heating up to about 265° F. and that when distilled with steam at below 265° F. there is no danger of corroding the equipment. It may, however, decompose on heating or on exposure to light in the presence of oxygen unless antioxidants are present.

In commercial practice the oil is blended with from  $\frac{2}{3}$  to  $1\frac{1}{2}$  volumes of trichloroethylene in a mixing column at about 100-120° F. The solution is chilled at the rate of 10-15° F. per hour although in exceptional cases the rate may be lowered to about 8° F. per hour. Sometimes it appears desirable to chill to +32° F. at the rate of 9° F. per hour and then increase the rate to 14-15° F. per hour. In order to obtain an oil of 0° F. pour test, the oil solution is usually chilled to -20° F. although this 20° F. differential may vary with the properties of the stock to be dewaxed or the pour test of the oil desired. The chilling operation can be thus accomplished in approximately 10 hours.

The chilled solution is charged to centrifuges which are vapor-tight and differ in the design from the conventional type of centrifuges. The semi-solid wax is discharged from the central part of the bowl into a steam heated wax receptacle whereas the dewaxed solution is discharged

into a carefully heat insulated receptacle and used for precooling the fresh oil-solvent blend. Because of the considerable difference in gravity between the oil and wax phases when trichloroethylene is employed as the dewaxing solvent the centrifuges can be operated at relatively low speeds of 8,000-9,000 r.p.m., instead of 15,000-17,000 r.p.m., when naphtha is used. Trichloroethylene is removed from the oil and wax phases by distilling at about 230° F. first in the absence and then in the presence of steam.

### *Bari-Sol Dewaxing Process*

The process has been developed by the Sharples Specialty Co., and Max B. Miller and Co., Inc. It is now being used commercially by the Continental Oil Co. The process employs a mixture of solvents, namely, benzol and ethylene dichloride. The properties of benzol were enumerated on page 58 while those of ethylene dichloride are given in the following table.

TABLE 12—Physical Properties of Ethylene Dichloride

|   |        |
|---|--------|
| Molecular weight ( $C_2H_4Cl_2$ ) ..... | 98.95  |
| Specific gravity .....                  | 1.257  |
| Boiling point, ° F. ....                | 182.7  |
| Melting point, ° F. ....                | — 31.5 |
| Solubility in water at 100° F., % ..... | 0.90   |

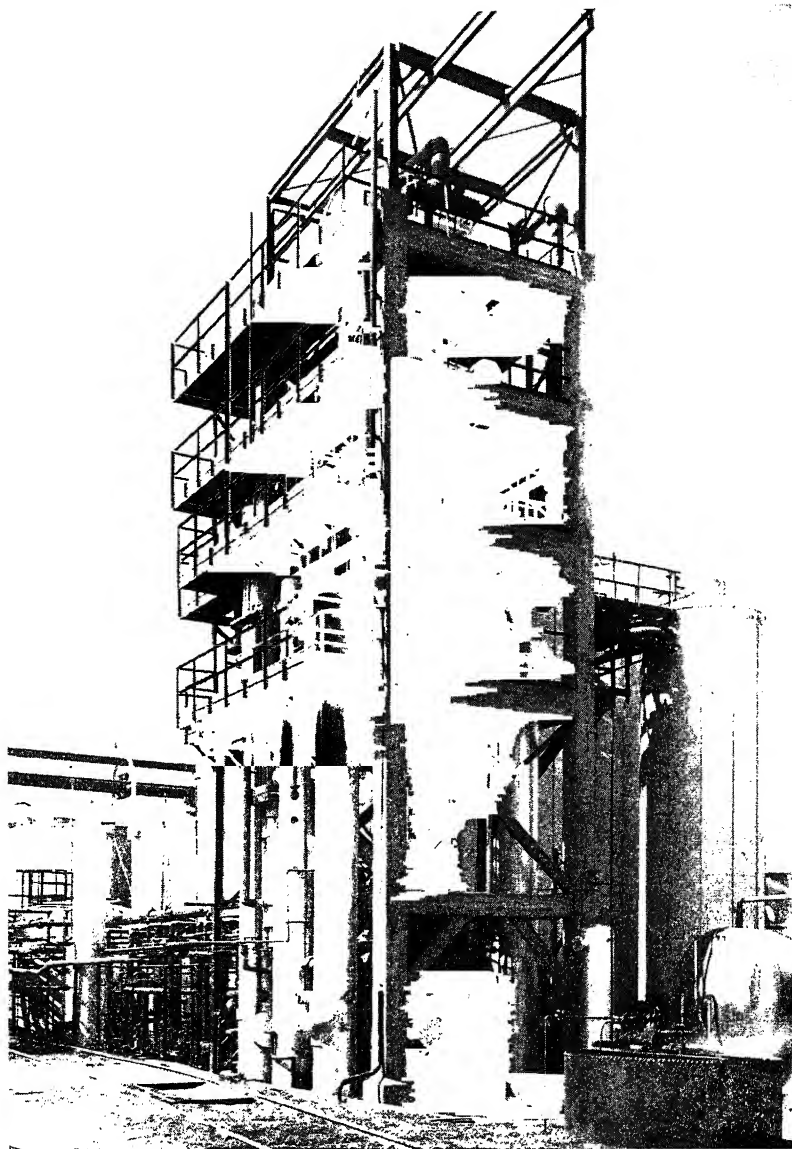
The solvent used commercially by the Continental Oil Co. contains 78% of ethylene dichloride and 22% of benzol by volume though obviously the composition may vary with the type of stock to be dewaxed.\* Addition of benzol is required as ethylene dichloride has insufficient solvent power towards the oil constituents and tends to precipitate some of the oil at the low chilling temperatures in a somewhat selective manner.†

In commercial operation the oil is blended with about 3 volumes of the solvent mixture in an agitator at approximately 110° F. The solution is chilled by passing it through the heat exchangers and then through the direct ammonia expansion chilling machines, the rate of chilling being of relatively minor importance. The chilling temperature is about —8° F. to —12° F. in dewaxing Mid-Continent stocks to a 0° F. pour test.

After centrifuging the wax phase is diluted with further quantities of chilled solvent, the resulting mixture containing approximately eight volumes of solvent per one volume of wax. This mixture is recentrifuged at a somewhat lower temperature than that employed in primary centrifuging, or at about —15° F. in the example given above. This is made possible by prechilling the solvent used for further dilution of the wax phase to a temperature of about —20° F. before blending. The wax is

\* The Continental Oil Co. plant is described by Albright.<sup>98</sup>

† Goldberg, Abezgauz, and Margolis,<sup>99</sup> discuss the solubility characteristics of ethylene dichloride.



*Courtesy: Max B. Miller and Co., Inc.*

PLATE III.—Bari-Sol Solvent Dewaxing Unit.

then recovered and the solvent containing the oil is used together with the fresh solvent for diluting the new oil charge to primary centrifuges. The solvent is recovered from the oil and wax phases at a temperature of about 290° F.

### Dewaxing with Various Organic Solvents

Besides the solvents described, a variety of other organic solvents can be employed for dewaxing purposes. These dewaxing solvents up to the present time have not found wide commercial application, but some of them appear to have considerable promise. This is particularly true for solvents which, under somewhat modified conditions of treatment, may be employed both as dewaxing and as deasphalting or solvent refining agents. The advantage of using such solvents commercially is self-evident as it becomes unnecessary to remove the solvent between the individual steps of refining.

In discussing the benzol-acetone dewaxing process it has been pointed out that the use of a mixture of solvents has some definite advantage over the use of single solvents by making the operations of the plant more flexible. Besides the benzol-acetone combination other similar combinations are possible, however, where acetone is replaced by one of the solvent refining agents such as liquid sulfur dioxide,<sup>100</sup> chlorex,<sup>101</sup> furfural,<sup>102</sup> aniline,<sup>103</sup> benzaldehyde,<sup>104</sup> nitrobenzene,<sup>105, 106</sup> etc.

Besides nitrobenzene, nitromethane, quinoline, furfural and chlorex are also specified as primary solvents, while carbon disulfide, various aliphatic alcohols, aliphatic amines and *iso*-pentane are enumerated among secondary solvents; Standard Oil Development Co.<sup>107</sup> specifies nitrobenzene, *o*-chlorophenol, benzaldehyde, phenols, phenol esters, cresols, methyl *iso*-butyl ketone, epichlorohydrin, ethylene dichloride, *iso*-propyl alcohol, pyridine and secondary amyl alcohol as primary solvents and toluene, xylene, tetralin, cyclohexane, *iso*-propyl ether, *o*-dichlorobenzene, gasoline, aromatic fractions of kerosene from solvent extractions as secondary solvents; N. V. de Bataafsche Petroleum Maatschappij<sup>108</sup> recommends a mixture of naphtha with furfural, aniline, aliphatic acids, esters, alcohols, ketones or carbonates; Govers<sup>109</sup> uses acetone and benzol for dewaxing and then a similar mixture, but containing larger quantities of acetone for solvent refining.

Of the above processes the benzol-liquid sulfur dioxide process both for dewaxing and solvent refining has reached the commercial state of development. By employing these solvents the oil can first be extracted by removing the low viscosity index constituents with mixtures containing relatively higher proportions of liquid sulfur dioxide and then dewaxed by increasing the benzol content of the raffinate phase and chilling to proper dewaxing temperature followed by the filtering operation. It is likewise possible, however, first to employ the proper benzol-liquid sulfur dioxide mixture for dewaxing and then to add sufficient quantities of liquid sulfur dioxide to the raffinate for separating the low viscosity index constituents at normal temperatures. In employing solvents, such as furfural or chlorex, the operation is similar: the oil is first extracted with such solvents for separating the low viscosity index con-

stituents, and the raffinate phase is then diluted with benzol and, if necessary, with additional quantities of the refining solvent. The possibilities of using such combinations commercially are illustrated by the following experimental data obtained in dewaxing a Mid-Continent residuum of 50 Saybolt Universal seconds at 210° F., with three volumes of various furfural-benzol blends at -5° F.

TABLE 13—Dewaxing with Blended Solvents  
(3 Volumes of Solvent per 1 Volume of Oil)

| Solvent Mixture |          | Dewaxed Oil<br>% Yield | Pour Test<br>° F. |
|-----------------|----------|------------------------|-------------------|
| % Furfural      | % Benzol |                        |                   |
| 5               | 95       | 82                     | 25                |
| 10              | 90       | 82                     | 20                |
| 20              | 80       | 77                     | 5                 |
| 30              | 70       | 57*                    | 0                 |

\* Two liquid phases are formed. Yield refers to the oil phase after removing the wax.

Extraction of the same oil with three volumes of a 35% acetone and 65% benzol mixture gave a yield of 78% of the dewaxed product of a +10° F. pour test.

The above data show that within the limits of experimental error the yield and properties of the oil dewaxed with benzol-acetone or with a mixture containing 20% furfural and 80% benzol are the same. Similar to the conditions encountered in benzol-acetone extractions, the decrease in the quantity of furfural in the furfural-benzol blend results in higher differentials between the pour test of the oil and the chilling temperature and in lower filtering rates. The use of excessive quantities of furfural, however, separates the oil into two liquid phases which can be expected with any solvent used for removing the low viscosity index constituents.

Solvents which can be used both as dewaxing and deasphalting agents are represented, besides propane, which was already discussed, primarily by the aliphatic alcohols. Their deasphalting properties are discussed in the later chapters and the present description refers only to their dewaxing characteristics.

In general, alcohols suitable for dewaxing are butyl, amyl or hexyl alcohols and their mixtures with lighter alcohols or other solvents. Addition of such solvents is frequently indispensable in order to modify the solubility characteristics so as to avoid excessive losses of the heavy oil fractions by preferential solubility.

Experimental data presented in Figure 5 show the results obtained in dewaxing a Mid-Continent residuum of 100 Saybolt Universal seconds at 210° F. and a pour point of 100° F. with various quantities of fusel oil\* at different temperatures. The relatively low yields of the dewaxed oil are to a great extent explained by the simultaneous precipitation of

\* Fusel oil used in these experiments contained approximately 70% *iso*-amyl alcohol and 30% of other alcohols, including different isomeric amyl alcohols, *iso*-butyl alcohol and a small amount of *n*-propyl alcohol.

asphalt as the primary purpose of these experiments was the determination of the overall effect of fusel oil extractions on the pour point of the oil. Undoubtedly, precipitation of the heavy oil fractions also occurred, which is frequently observed with other solvents of the similar type.

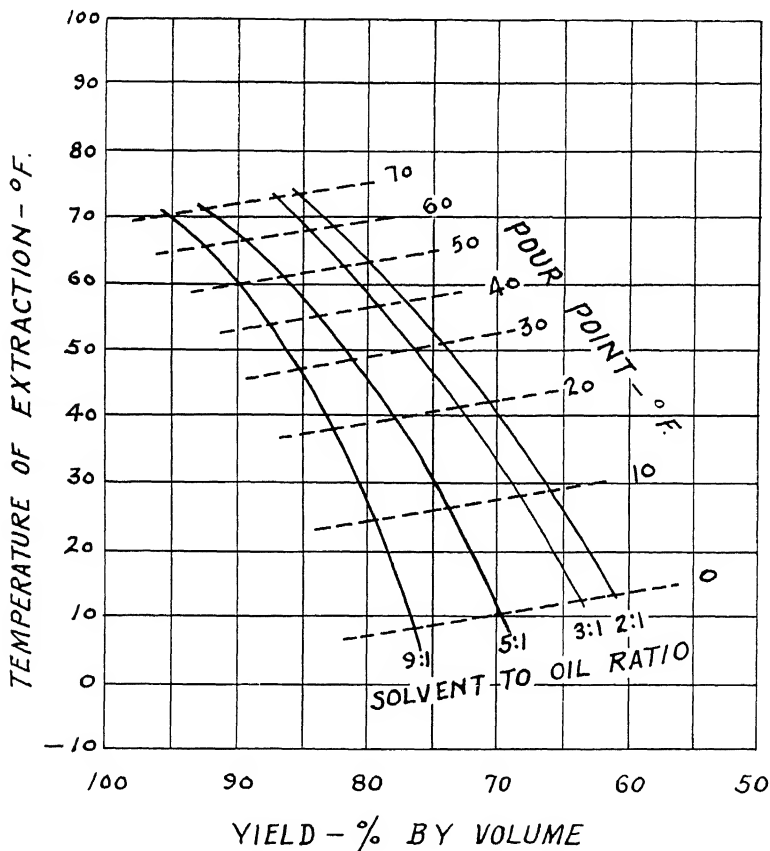


FIGURE 5.—Effect of Treating Conditions on the Yield and Pour Point of a Mid-Continent Residuum (Batch Extractions with Refined Fusel Oil).

It can be noted from the data plotted on Figure 5 that the pour test of the dewaxed oil is generally equal to but usually lower than the chilling temperature, which is particularly noticeable in dewaxing the oil to higher pour tests. This negative differential decreases as the quantity of fusel oil used is increased. The high solvent ratios must be employed, however, in order to improve the yield of the dewaxed oil. The data are characteristics of alcohols in general and of the various types of oils to be

dewaxed although the relative importance of the different factors involved in dewaxing may vary to a considerable extent.

The possibility of utilizing alcohols as dewaxing solvents has been realized for some time. The following articles and patents are of interest in this connection: Poole and Collaborators<sup>110</sup> determined solubilities of oil and wax in various alcohols as well as in other organic solvents; I. G. Farbenindustrie A.-G.<sup>111</sup> recommends butyl alcohol for dewaxing purposes; Smith<sup>112</sup> investigated secondary butyl alcohol alone and in combination with acetone; Govers<sup>113</sup> dewaxes oils with a mixture of amyl alcohol and aniline; Lane<sup>114</sup> uses mixtures of butyl alcohol and acetone; Govers<sup>115</sup> employs tertiary butyl alcohol; etc.

A very large variety of other organic solvents which may or may not have more or less pronounced solvent refining and deasphalting characteristics has been proposed for dewaxing purposes alone or in combination with other modifying solvents. The work of Poole<sup>116</sup> has been particularly extensive in this connection and indicated that, besides butanol and Pentasol, butyl formate and paraldehyde are particularly

TABLE 14—Solvent Dewaxing Plants in Operation or Under Construction

| <i>Benzol-Ketone (Benzol-Acetone) Process</i> |                      |                                 |
|---|----------------------|---------------------------------|
| Company                                       | Location             | Charging Capacity<br>(Bbls/Day) |
| Indian Refining Co. ....                      | Lawrenceville, Ill.  | 1,850                           |
| Atlantic Refining Co. ....                    | Philadelphia, Pa.    | 750                             |
| Gulf Oil Corp. ....                           | Port Arthur, Texas   | 1,600                           |
| Herbert Green Co. ....                        | East Halton, England | 1,000                           |
| Deutsche Vacuum Oel A.-G. ....                | Bremen, Germany      | 500                             |
| Raffineria di Napoli, S.A.I. ....             | Naples, Italy        | 500                             |
| Socony-Vacuum Oil Co., Inc. ....              | Paulsboro, N. J.     | 3,800                           |
| Shell Mex and B.P. ....                       | Shell Haven, England | 1,170                           |
| Gewerkschaft Elwerath ....                    | Hannover, Germany    | 1,700                           |
| The Texas Co. ....                            | Port Arthur, Texas   | 2,500                           |
| S.A. Petrofina ....                           | Dunkerque, France    | 500                             |
| Quaker State Refining Co. ....                | Pennsylvania         | 1,000                           |
| Socony-Vacuum Oil Co., Inc. ....              | Olean, New York      | 1,500                           |
| Magnolia Petroleum Co. ....                   | Beaumont, Texas      | 3,000                           |
|   |                      | 21,370—67.2%                    |
| <i>The Propane Process</i>                    |                      |                                 |
| Standard Oil Co. Indiana ....                 | Wood River, Ill.     | 1,300                           |
| Union Oil Co. ....                            | Oleum, California    | 2,000                           |
| Shell Petroleum Co. ....                      | Wood River, Ill.     | 2,400                           |
| Bradford Penn. Refining Co. ....              | Warren, Pa.          | 250                             |
| Kendall Refining Co. ....                     | Bradford, Pa.        | 1,200                           |
|   |                      | 7,150—22.4%                     |
| <i>The Bari-Sol Process</i>                   |                      |                                 |
| The Standard Oil Co. La. ....                 | Baton Rouge, La.     | 2,000                           |
| The Continental Oil Co. ....                  | Ponca City, Oklahoma | 500                             |
|   |                      | 2,500—7.8%                      |
| <i>The Trichloroethylene Process</i>          |                      |                                 |
| Standard Franco Americaine ....               | Port Jerome, France  | 850—2.6%                        |
| Total   |                      | 31,870—100%                     |

promising. Esters are the subject of a large number of patents on dewaxing solvents. Ethyl esters of organic acids boiling above acetic acid, as represented by ethyl butyrate, valerate, *iso*-valerate, propionate, or their mixtures boiling, preferably, between 185-315° F., alone or in combination with benzol, naphtha, carbon disulfide, toluol, carbon tetrachloride, or pyridine, have been recommended.<sup>117</sup> Acetates,<sup>118</sup> formates and carbonates,<sup>119</sup> as well as other similar compounds,<sup>120</sup> are patented. Ethers might be also utilized for dewaxing purposes<sup>121</sup> as well as a series of other organic solvents.<sup>122</sup>

The above discussion shows that a large number of organic solvents are suitable for dewaxing of petroleum oils and that proper selections can be made for satisfying the particular needs of individual refiners. It is likewise evident that solvents now employed commercially are those which are at the present time most economical, but that these economical considerations may undergo certain changes in the future when new solvents may be introduced on the market.

### Solvent Dewaxing Plants

The tabulation on page 68 shows charging capacities of the existing solvent dewaxing plants, and their distribution between the various oil companies.<sup>123</sup>

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## Chapter VI

### Removal of Oil from Petroleum Waxes

Waxes removed from petroleum oils by the methods described in the preceding chapters always contain more or less oil which must be separated from the wax before it is placed on the market.\*

This problem is in some respects different from that encountered in the dewaxing of petroleum oils as the quantity of oil present in the wax is relatively small. For this reason, the methods employed in deoiling waxes and in dewaxing oils are not necessarily alike.

#### Deoiling Paraffin Waxes

As already described in the previous chapters, refinery waxes can be divided into two distinct groups: paraffin waxes and ceresins. Due to the differences in their characteristics the methods for deoiling them are different and are, for this reason, described separately.

##### *Sweating*

Paraffin waxes are characterized by their inability to retain large quantities of oil. Oil can be easily separated from the solidified wax by gradually raising the temperature of the wax cake and allowing it to drip from the wax crystals. This rather primitive method of separating the oil, known as "sweating," is employed by most of the refineries, being in many instances more economical than the more modern methods of accomplishing the same purpose by extraction with solvents.

The sweating process<sup>1</sup> consists in transferring the "slack wax," or the wax obtained directly from the dewaxing processes, into large pans, chilling it so as to obtain a solid wax cake, and then gradually raising the temperature in order to collect the different fractions as they become gradually liquefied by the application of heat. The sweating pans are usually from 20 to 60 feet long, from 8 to 10 feet wide, and about 8 inches deep so as to form a wax cake of approximately 6 inches in thickness. Wax is supported on these pans by means of wire screens, with provisions made for free draining of the fractions as soon as they become liquid. Cooling and heating of the wax cake is effected by passing cold or hot water through the coils located above the screens supporting the wax cake but below the surface of the cake. In normal operation the pans

\*"Vaseline" and similar products which contain certain quantities of added oils are not considered in this discussion.

are first filled with water to a depth just sufficient to cover the screen and the hot wax is then pumped into the pans until the desired thickness of the wax layer is obtained. The hot liquid wax is solidified by pumping cold water through the coils, the rate of chilling having, apparently, no effect on the sweating properties of the wax. After a solid cake is obtained the water is drained from the bottom of the pans and the temperature of the cake now supported by the screen, is then gradually raised either by circulating warm water through the coils or by heating the chamber or "oven" where the pans are located with special steam coils outside of the pans. The rate of heating the wax cake is highly important in order to obtain the cleanest possible separation of oil from the wax. This is illustrated by the following data obtained in laboratory experiments using a Mid-Continent slack wax of 112° F. melting point, and a 32% oil content. In commercial practice the usual rate of heating the wax cake is approximately 1° F. per hour.

TABLE 15—Effect of Rate of Heating in Sweating

| Rate of Heating<br>° F./Hr. | Yield<br>% Wt. | Melting Point<br>° F. | Oil Content<br>% Wt. |
|-----------------------------|----------------|-----------------------|----------------------|
| 1                           | 20             | 129.0                 | 0.15                 |
| 2.5                         | 20             | 128.4                 | 0.39                 |
| 5                           | 20             | 127.7                 | 0.63                 |
| 10                          | 20             | 126.8                 | 1.00                 |
| 1                           | 15             | 128.0                 | 0.10                 |
| 2.5                         | 19             | 128.0                 | 0.38                 |
| 5                           | 22             | 128.0                 | 0.80                 |
| 10                          | 25             | 128.0                 | 1.80                 |

The drippings from the pans are usually collected in two separate fractions: the first fraction consisting primarily of oil and low melting point waxes known as "foots oil" and the second fraction or the "intermediate cut" being a mixture of relatively small quantities of oil, large quantities of low melting point waxes, and some of the high melting point waxes. The wax remaining on the pans or "scale wax" is then removed by melting it by circulating hot water through the coils. This wax is then refined in the usual manner by percolating or contacting with clay with or without prior refining with sulfuric acid, sodium hydroxide, or other refinery reagents.

The wax structure is of considerable importance in successful operation of the sweating processes. As already mentioned in the previous chapters best results are always obtained with the needle crystals which permit an easy removal of the melted portions from the main body of the crystals by draining. For this reason, inspection of the slack wax cake permits one to draw definite conclusions with respect to the ease with which it can be sweated.

Although the process is very inefficient, the quantity of the recoverable products can be greatly increased by introducing suitable recycling opera-

tions. The intermediate cut is usually blended with the fresh charge of the slack wax in order to increase the recovery, or a highly complicated system of recycling may be employed if the refinery is interested in obtaining a variety of waxes of different melting points.

This conventional method of separating oil from the paraffin wax remained practically unaltered for a number of years with the exception of certain mechanical improvements in the sweating equipment. Recently, however, suggestions have been made to modify the process by saturating the wax cake with various solvents such as chlorex,<sup>2</sup> solvents rich in aromatics,<sup>3</sup> etc., in order to facilitate the ease of separating the oil from the wax. In applying such processes, however, a careful economical balance should be made in order to determine whether the cost involved in separating the solvent from the resulting products and the inevitable solvent losses are counterbalanced by the additional recoveries of the sweated products.

### *Solvent Pressing*

From the above it follows that the separation of oil and low melting point waxes from the high melting point waxes is accomplished by fractional melting, a process which is known to be theoretically inefficient. For this reason, other processes were recently proposed which involve the principle of fractional crystallization. These processes involve the use of solvents such as naphtha, benzol-acetone, etc., which were mentioned in connection with the dewaxing of petroleum oils. The wax is dissolved in the solvent at a somewhat elevated temperature, the mixture is chilled and the solvent with the dissolved oil is separated from the crystallized wax by pressing. The quantity of solvent used usually varies from  $\frac{1}{2}$  to  $1\frac{1}{2}$  by volume of the slack wax and pressures employed for separating the solidified wax from the solvent-oil solution may be as high as 300 lbs. per sq. in. or more.\*

The fractional crystallization processes were employed by the petroleum industry at an early date. The crude paraffin was mixed in the molten state with light petroleum fractions, allowed to solidify, cut into sheets and pressed to remove the solvent and the oil. See Pyhaelae.<sup>4</sup>

It has been abandoned, however, at this time due to its expensiveness.

The pressing processes for deoiling waxes always yield considerably larger quantities of waxes of a given melting point and oil content than the sweating methods. Thus sweating of a 112° F. melting point slack wax of a 32% oil content obtained from Mid-Continent crude yielded 20% of scale wax of a 128.4° F. melting point and a 0.15% oil content. By blending the above slack wax with  $\frac{2}{3}$  volume of naphtha, chilling the mixture to 60° F. and pressing at this temperature, the yield of the wax of the above melting point and oil content specifications was raised to

\* Hausmann,<sup>5</sup> compares the advantages and disadvantages of the sweating and pressing methods for deoiling waxes.

39%. This high recovery could not be reached by sweating even on repeated recycling operations.

In separating oil from the wax by solvent pressing the quantity of solvent required depends on the quantity of oil present in the wax and the conditions of pressing. Irrespective of the thoroughness of the pressing operation, a certain quantity of solvent is always retained by the wax cake and after distilling it from the wax the proportionate quantity of the oil dissolved by this solvent will be left in the wax. For this reason, the adjustment of the actual conditions of pressing with respect to the quantity of solvent required should be studied in each individual case as it depends on the nature of the pressing equipment used and the specifications for the finished product.

The pressing temperature determines the melting point of the recovered wax. It is, therefore, also adjusted according to the refinery requirements. Recycling is employed to a more or less considerable extent in order to obtain waxes of different melting points or to increase slightly the yields which may become of some significance when the ratios of naphtha to slack wax are unusually high.

Considering the commercial applicability of the pressing operations it should be noted, however, that waxes from different crudes differ in their pressing qualities. Some of them may form slimy cakes which are difficult or even impossible to press. It should be also noted that the necessity of using solvents increases the operating costs and, for these reasons, a careful investigation is always required before the method of deoiling paraffin waxes is finally adopted for plant use.

A few other methods have been recommended for separating oil and various melting point waxes into fractions such as contacting the crude slack wax with a moving stream of alkali phosphate,<sup>6</sup> treating the wax with water containing a wetting agent of the type of an aromatic sulfonic acid,<sup>7</sup> etc., but these methods up to the present time are of little commercial significance.

### **Deoiling Ceresin Waxes**

Ceresin waxes cannot be sweated due to their inability to form well defined and large crystals and to the ease with which they occlude the oil. For this reason, the oil is separated from them by means of solvents. Both filtering and centrifuge methods might be resorted to in accomplishing the separation of the solvent and wax, but the centrifuge methods are most commonly used.

Goldberg and Abezgauz<sup>8</sup> describe the use of centrifuges for separating ceresin waxes from petrolatum and compare the results with those obtained by the Weir process and by cold settling. The latter process is claimed to be unsatisfactory because of excessive time, large volumes of naphtha required and low chilling temperatures. Sachanen<sup>9</sup> also describes separation of ceresins from petrolatum by various methods.

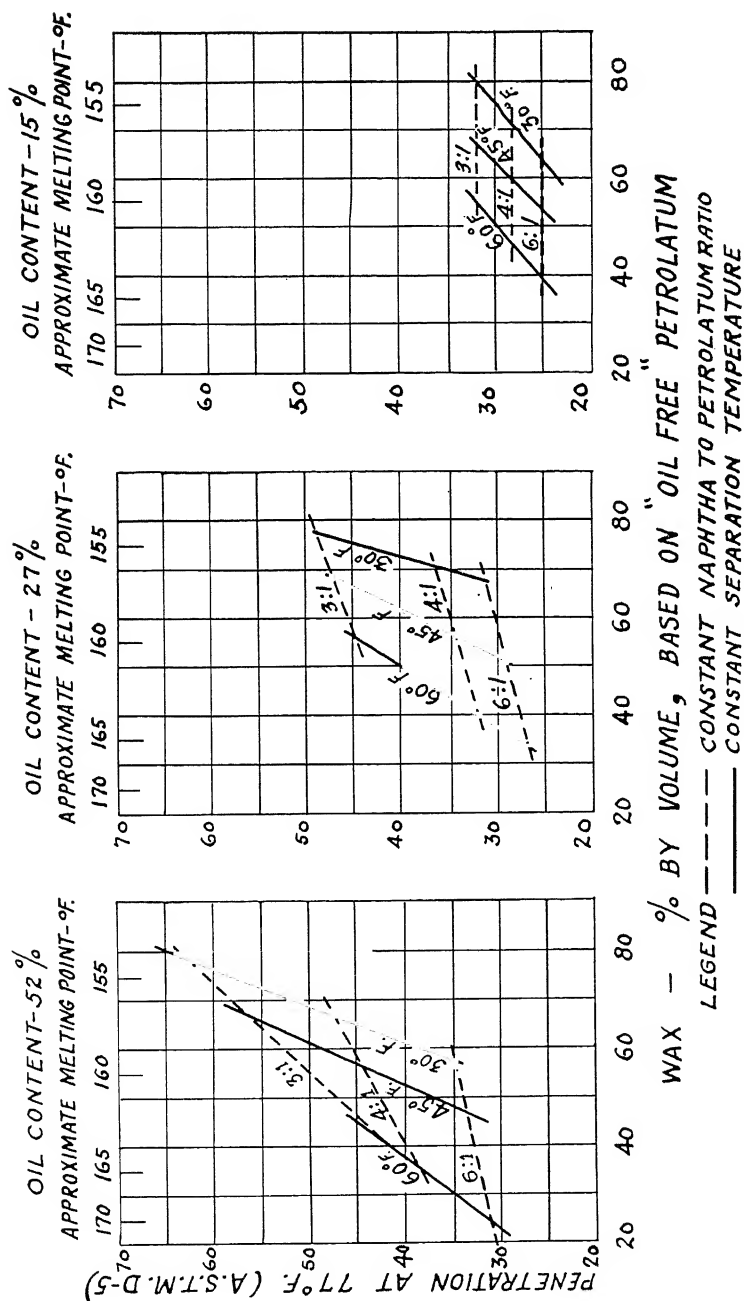


FIGURE 6.—Effect of Temperature, Naphtha Dilution, and Oil Content of Petrolatums from Mid-Continent Residua on the Yields and Properties of Separated Waxes.

In commercial practice petrolatums obtained in dewaxing petroleum oils are blended with three to five volumes of naphtha and chilled to temperatures necessary for obtaining the wax of desired melting point. The factors influencing the solvent ratios and the separation temperatures are the same as those described in solvent pressing of paraffin waxes. It should be mentioned, however, that petrolatums are usually differentiated not by their oil contents directly, but rather by their penetration characteristics which are an indirect measure of the oil content. In general, high separation temperatures and naphtha to petrolatum ratios decrease the yields, raise the melting points and lower the penetration characteristics of the finished products. As naphtha, as well as other solvents, is usually more selective at lower than at higher temperatures it is, generally, preferable to control the melting point of the ceresin wax by selecting the proper separation temperatures, and the oil content (or penetration) by adjusting the naphtha to petrolatum ratio.

The interdependence of the variables involved in separating ceresins from petrolatums in naphtha solution is shown in Figure 6. Petrolatum from a solvent treated Mid-Continent residuum was chosen for these experiments which were made in laboratory equipment. In order to permit the plotting of the results on a common basis, yields are expressed as percentages of "oil-free" petrolatum (oil containing petrolatum recovered divided by oil free petrolatum charged), or petrolatum present in the corresponding oil mixtures after analytical extraction of the oil with benzol-acetone solutions. Such "oil-free" petrolatum had a melting point of 148° F. The naphtha ratio is based on oil bearing petrolatum charged.

A closer inspection of the data shows that lowering of the oil content of the petrolatum improves the penetration characteristics of ceresin waxes, minimizes the effect of naphtha dilution, but has no appreciable effect on the yield-melting point relationship of the resulting products. This should be expected as the amount of oil left in the wax layer is proportional to the oil concentration in the naphtha solution, which in its turn is determined by the oil content of the petrolatum. The effect of the oil content of petrolatum on its penetration has already been mentioned. The interdependence of other variables investigated in this work can easily be observed by inspecting the presented graphs.

The above discussion gives a general outline of the existing methods for separating oil from petroleum waxes. As mentioned in the beginning of this chapter many of them are similar to those employed for separating wax from oil and, in order to avoid unnecessary repetitions, further discussion of the subject is superfluous.

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## Chapter VII

### Asphaltic Substances

Asphaltic substances present in petroleum oils are generally considered as undesirable constituents because they have an unfavorable effect on the carbon residue or coke number, and color of the oil. They are likewise held responsible for carbonization and instability of oils in service and, for these reasons, their removal from the oil is believed to be desirable.

#### Nature of Asphaltic Substances

The exact nature and characteristics of asphaltic substances present in petroleum is not well known notwithstanding the considerable amount of research work which has been conducted along these lines in the past. Due to their complex nature they cannot be analyzed by the conventional chemical methods and their separation into different classes is accomplished on the basis of their preferential solubilities in various solvents. The choice of solvent or of conditions of extraction tends, however, to shift the demarkation line between the different classes of these compounds, and although the definition of the characteristic types of such substances presents no particular difficulty, it is impossible to draw definite dividing lines between the substances which fall on the borderlines between two adjacent classes. It is equally impossible to make a sharp differentiation between the asphaltic substances and the oil constituents although this can be accomplished in an arbitrary manner by some of the proposed analytical methods.\*

The possibility of separating petroleum into different fractions by preferential solubility in solvents can be ascribed apparently to Jacobsen<sup>5</sup> who observed the separation of asphalt on diluting heavy petroleum oils with the light petroleum fractions. It was later found by Holde that the amount of precipitate formed on such dilution depends both on the quantity and the gravity of the light petroleum fractions used as diluents.<sup>6</sup> Richardson<sup>7</sup> made use of these observations in developing a method of analyzing asphaltic substances and separating them into "hard asphalt" and "soft asphalt" by their relative solubilities in various hydrocarbon

\* For complete discussion of asphalt and related substances see Abraham;<sup>1</sup> Sachanen;<sup>2</sup> Marcusson, Burchartz, and Wilke;<sup>3</sup> see also Kalichevsky and Fulton,<sup>4</sup> who give a brief review of the foreign literature on this subject.

solvents, while Marcusson<sup>8</sup> introduced further improvements in this method which is now rather universally adopted by the industry.\*

The highly interesting and enlightening work of Sachanen and his collaborators<sup>9</sup> gave a better insight into the physico-chemical phenomena which are involved in the above reactions. They showed that asphaltic substances present in the oil form colloidal solutions and that the problem of separating them from the oil or of keeping them in proper suspension is one of colloidal chemistry. The exact chemical nature of these compounds is not yet accurately known and it is not yet definitely established whether traces of elements other than hydrogen and carbon, such as oxygen, are essential for imparting to them the required chemical structure. By separating them in the order of their solubilities in various solvents, the asphaltic bodies can be divided into the following general groups, their hydrogen to carbon ratio increasing with the increase in their solubilities in the following order:

*Carboids*—substances insoluble in all organic solvents including carbon disulfide,

*Carbenes*—substances insoluble in benzol but soluble in carbon disulfide,

*Asphaltenes*—substances insoluble in petroleum ether but soluble in benzol,

*Resins*—substances soluble in petroleum ether but retained from the petroleum ether solutions on percolating them through clay.

Resins are gradually converted into asphaltenes through the loss of hydrogen due to oxidation. Conversely, asphaltenes can be converted into resins by hydrogenation.<sup>10</sup>

Besides the above compounds, the oil or asphalt may also contain asphaltous acids or asphaltous acid anhydrides which, similarly to asphaltenes, precipitate on dilution of their benzol solutions with petroleum ether but which can be titrated or saponified with alkali hydroxides.

In general, carboids and carbenes are absent from most of the crude oils although they may form a substantial portion of asphaltic products which are obtained in the course of thermal decomposition. For this reason, further discussion concerns mainly asphaltenes, resins and their solutions in mineral oils.

In considering the system asphaltenes—resins—oil, Sachanen postulates that asphaltenes, unlike paraffin wax, are colloids which are so finely dispersed in the oil that it is often impossible to detect individual particles even with an ultra microscope.† Asphaltenes are further considered

\* For details of Marcusson's method of analyzing asphalts see Kalichevsky and Fulton.<sup>4</sup>

† The colloidal nature of asphaltic solutions in oil has been also suggested by Schneider and Just.<sup>11</sup>

to be lyophilic with respect to aromatic hydrocarbons and allied solvents in which they are highly dispersed and stable. The apparent solubility of asphaltenes in kerosene or other solvents of a similar nature is due to occluded resins always present in asphaltenes unless they are subject to extensive purification. These resins act as protective colloids as the asphaltenes freed from resins are incapable of being dispersed even in such high boiling solvents as kerosene.

The colloidal nature of asphaltenes is substantiated by researches of other investigators. Thus, according to Nellensteyn,<sup>12</sup> a filtered solution of natural asphalt in toluene shows Brownian movement with 160x magnification while at 1000-2000x magnification the particles appear differently colored. Zaharia and Lucatu<sup>13</sup> were able to separate asphaltenes from resins and paraffin wax by diffusion through porous membranes. As asphalt is composed of asphaltenes and similar substances dispersed in the oil with resins acting as protective colloids, high grade asphalts can be produced by adjusting proper mixtures of these three components in order to obtain high grade asphalts (Fulton and Kalichevsky,<sup>14</sup> and Standard Oil Development Co.<sup>15</sup>).

By accepting this theory of the colloidal nature of asphaltic substances present in the oil it can be readily seen that in diluting heavy mineral oils with light hydrocarbon solvents the resins lose their protective properties towards asphaltenes depending on the decrease in the molecular weight of the solvent and the degree of dilution. This determines the relative quantities of the asphalt which are precipitated from the oil by a given solvent under the experimental conditions employed. It can be also assumed that the lighter the hydrocarbon solvent the greater is the number of substances present in the mineral oil which behave as colloids with respect to this solvent.

The colloidal theory of mineral oils containing asphalt does not preclude the possibility that mineral oils contain also substances which form true solutions in light hydrocarbon solvents but which are not completely miscible with these solvents. The relative quantities of such substances separated from the oil on dilution with light hydrocarbons should also depend on the nature of the solvent, solution temperature, degree of dilution, and other variables controlling the solubility phenomena. If it be assumed that the relative solubility of such substances in light hydrocarbons is more or less related to their molecular weight, it is natural to expect that the components progressively thrown out from the solution will be generally similar to fractions obtained by distillation.

### **Asphaltic Substances in Solvent Refining**

The above discussion presented the accepted methods for analyzing and classifying asphaltic substances on the basis of their solubility characteristics. The problem has a somewhat different aspect, however, when the classification is made from the viewpoint of solvent refining assuming that the asphalt content of an oil is directly related to its carbon residue or coke number characteristics.

In removing the asphaltic substances from a Mid-Continent residuum of 144 Saybolt Universal seconds at 210° F. and a carbon residue of 3.5 with refined fusel oil, which is a deasphalting agent as discussed in the later chapters, the carbon residue could not be reduced below 2.2 irrespective of the conditions of extraction or the quantity of solvent used. In removing the asphaltic substances from the same oil by careful laboratory distillation the carbon residue of the resulting distillate has been found to be 2.0 or practically the same as in fusel oil extractions. The same limit was obtained in precipitating the asphaltic substances with propane. This indicates that the various deasphalting methods are capable of decreasing the carbon residue of an oil to approximately the same level irrespective of the method chosen for accomplishing this purpose. In these experiments the losses in deasphalting operations were, however, never below 10% or several times higher than the combined asphaltene and resin content of the oil as determined by the conventional analytical methods. These experiments, therefore, indicate that carbon residue is not necessarily directly related to the asphaltene and resin content of the oil.

The above experimental data likewise show that a distillate oil may still possess a high carbon residue although all precautions are taken in order to eliminate any possible entrainment in the distillation procedure. This is explained by the inherent differences in the two methods of distilling the oil. In determining the carbon residue the oil is distilled at atmospheric pressure and in presence of air which results in partial cracking of the heavy oil fractions and in their oxidation accompanied by the deposition of carbonaceous substances. In vacuum distillation, cracking is reduced to a minimum due to the low distillation temperatures, while the presence of air is also excluded. For these reasons, if asphalt is defined in terms of carbon residue, two types of asphaltic substances should be assumed to be present in the oil, which, following the nomenclature adopted for the gum content of gasoline, may be defined as "pre-formed" asphalt and "potential" asphalt. These two types of asphalt are in no relation, however, to the asphaltic substances as determined by Marcusson's analysis.

The picture is further complicated, however, if the asphaltic bodies are classified according to their ease of removal with the refining solvents. As mentioned in Chapter II, refining solvents are not efficient in reducing the carbon residue of the oil to low values. By applying these solvents to residual oils it is found that a certain minimum carbon residue is obtained and that further reduction of carbon residue beyond this minimum becomes impractical. The types of asphaltic substances removed by the deasphalting and solvent refining agents are different, however, as the carbon residue of a deasphalted oil is reduced still further by the refining solvents, while the carbon residue of a solvent refined oil can likewise be reduced by a subsequent deasphalting operation. Prob-

ably the existence of such two types of asphaltic substances might be explained on the basis of colloidal phenomena. It might be assumed that the asphaltic substances forming colloidal solutions are dispersed with relatively equal ease in the oil and in the refining solvents, while the asphaltic substances forming true solutions are removed from the oil by the preferential solubility in such solvents. The deasphalting solvents, on the other hand, are capable of precipitating such colloiddally dispersed particles while they have little if any preferential solubility effect towards constituents which are present in the oil in true solution. These two types of asphaltic substances have likewise no definite relation to the asphaltic substances as determined by Marcusson's analysis or to the so-called "preformed" and "potential" asphalts.

The rather indefinite borderline between the substances present in the colloidal state or in true solution makes the differentiation between the two types of asphaltic substances mentioned above somewhat vague. It shows, however, that the deasphalting agents are primarily capable of precipitating from the oil substances of high molecular weight which, from the refining viewpoint, may be sometimes identified as the heavy oil fractions. Such heavy oil fractions are not necessarily harmful when present in the finished products and, for this reason, the deasphalting operations should not be carried out to unnecessary extremes. If this is done, however, the deasphalting agents will remove not only the undesirable asphaltic bodies but also the desirable high viscosity and high boiling point oil constituents of high molecular weight but otherwise of satisfactory service characteristics.

The differentiation between the asphaltic substances which are easily removed by the deasphalting and by the refining solvents is not sharp, however. A very drastic deasphalting operation will remove some of the asphaltic substances which are also removed by solvents, while a drastic solvent refining operation will remove some of the asphaltic substances which are easily precipitated by the deasphalting agents. For these reasons, the deasphalting operation should be adjusted depending on the severity of the subsequent solvent refining step in order to obtain the maximum efficiency in the refining operation. In deasphalting an oil to various asphalt contents as determined by the carbon residues, it is noted, however, that a certain minimum exists below which the action of the refining solvent becomes rather ineffective in lowering the carbon residue of the oil. Thus by deasphalting a Mid-Continent residuum of 144 Saybolt Universal viscosity at 210° F. and a 3.5 carbon residue to a carbon residue of 3.1 the subsequent solvent extraction reduced its carbon residue to 1.5. However, when the same residuum was deasphalted to a carbon residue of 2.9 and treated with the same quantity of solvent under identical treating conditions the carbon residue was reduced to 0.7. The difference in the carbon residues of the deasphalted oils of 0.2 thus resulted in the difference of 0.8 in carbon residues of the

two oils after solvent refining. This can be, apparently, explained only by the assumption that the heavy asphaltic particles present in the oil are capable of associating with the asphaltic substances of lower molecular weight forming new complexes which are relatively inert to the action of refining solvents being of distinctly colloidal nature.

As already mentioned, the removal of asphaltic substances from petroleum oils improves their carbon residue and color characteristics. This does not assume, however, that all of the colored substances are of asphaltic nature and that for this reason the oil can be decolorized merely by removing the asphalt. It only implies that most of the asphaltic substances form colored solutions with the oil. For this reason, the improvement in the color of the oil in deasphalting operations is an indication but not necessarily a measure of the amount of asphaltic substances removed.

Besides carbon residue and color characteristics, removal of asphaltic substances is reflected in the change of some of the other properties of the oil. Viscosity is lowered considerably due to the removal of the high molecular weight constituents. The viscosity index of the oil may remain unchanged but is frequently lowered.\*

The pour test may also be affected as shown in Chapter III. The specific gravity of the oil is usually lowered while the viscosity-gravity constant shows in general only minor variations. The flash and fire points occasionally show a decrease.

\* The reasons for lowering the viscosity index in the deasphalting operations are explained in connection with the discussion of substances used for improving the viscosity index of oils.

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## Chapter VIII

### Conventional Deasphalting Methods

A number of commercial methods for removing the asphaltic substances were known by the petroleum industry before the appearance of the solvent deasphalting methods which are now gradually being adopted for processing the residual oils. Of these older methods distillation, refining with clay and sulfuric acid, and treatment of oils with various precipitating agents are the most important ones in connection with the solvent refining operations and are, for this reason, briefly described in this chapter.\*

#### Deasphalting by Distillation

From the very beginning of petroleum refining it was known that asphaltic substances can be separated from petroleum oils by distillation. For this reason, distillation should be considered as the first deasphalting process which was applied in practice. With the advent of solvent refining it has been also found that solvents are most effectively applied to distillate and not to residual oils and, although the exact reasons for such behavior of solvents may not have been clearly understood, the first solvent refining processes were confined only to the distillate stocks.

In deasphalting oils by distillation, difficulties are encountered, however, in separating all of the oil from the asphalt as the heavy petroleum fractions have a low volatility and, due to thermal decomposition, cannot always be obtained as distillates. These distillation problems are of relatively minor importance with the crudes of the Coastal type which have a comparatively low boiling point for a given viscosity, but they become increasingly difficult with the oils of Mid-Continent type while Pennsylvania oils cannot yet be satisfactorily distilled in commercial equipment without substantial cracking. Considerable progress in the distillation processes has been achieved, however, in the course of the last few years which opened the possibility of applying the distillation methods for deasphalting a number of crude oils of comparatively low volatility. The work along these lines is being continued by a number of industrial concerns as distillation is a relatively inexpensive operation and can compete successfully with the different physico-chemical deasphalting methods which were recently developed for refining such types of oils.

\* Chemical methods which may be employed for deasphalting, *i.e.*, decreasing the carbon residue, of petroleum oils are described in detail by Kalichevsky and Stagner.<sup>1</sup> The distillation methods are discussed by Bell.<sup>2</sup>

In separating heavy petroleum fractions from asphalt by distillation, the operation should be carried out at the lowest possible temperatures in order to avoid cracking. This can be accomplished by high vacuum distillations in the presence of large quantities of steam or similar carriers. If high distillation temperatures still cannot be avoided the time during which the oil is exposed to such temperatures is reduced to a minimum. A number of distillation processes embodying these principles have been developed in the course of the last few years such as the Lummus or Coubrough process, McKee distillation process, Alco Two Stage Distillation Process, Foster-Wheeler process, Mercury Vapor process, etc.\*

The introduction of high speed motors by the automobile manufacturers resulted, however, in an increased consumption of low viscosity oils which were previously of little commercial value. As a result some of the refineries are now faced with the overproduction of high viscosity oils and the possibility of converting them to low viscosity oils is, therefore, frequently attractive. For this reason, a certain amount of cracking in the course of distillation may be even desirable due to an increase in the yield of low viscosity oils from a given crude. This explains the present attempts to develop "viscosity-breaking" units for thermal treatment or distillation of petroleum oils containing the lubricating oil fractions. Application of similar methods for reducing viscosity of fuel oils has been well known for a number of years.

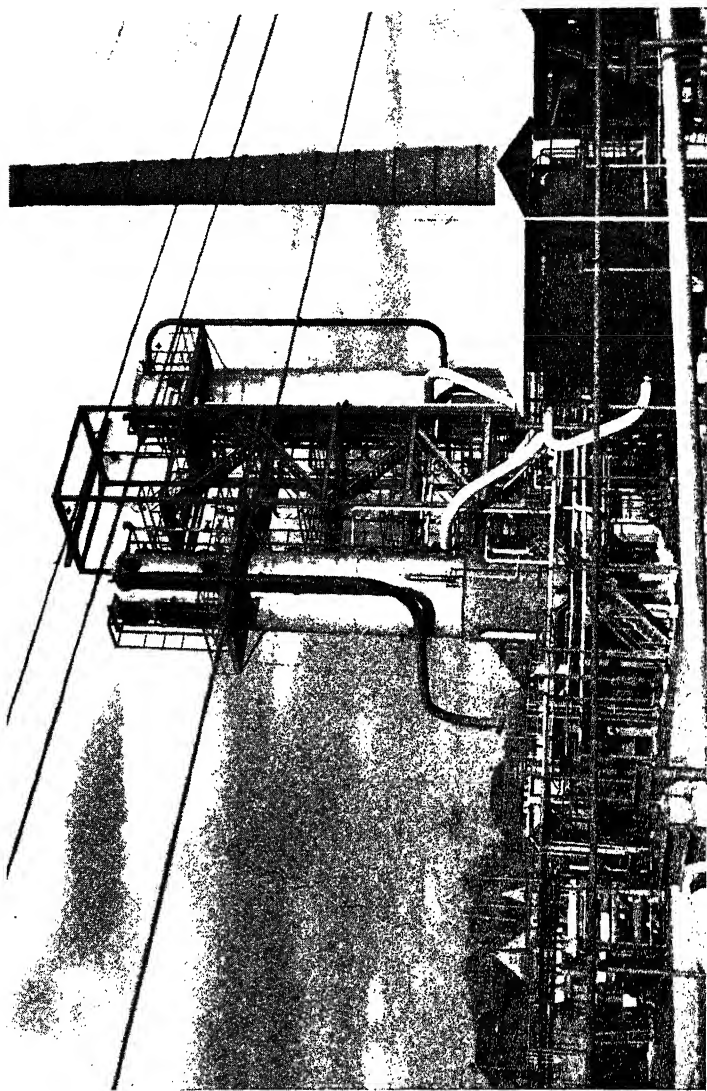
In these distillations two new principles which were recently patented by Bahlke and Stockdale of the Standard Oil Co. of Indiana,<sup>4</sup> and by Coubrough of the Lummus Co.,<sup>5</sup> are sometimes introduced in the design and operation of the equipment, increasing the content of the non-volatile asphaltic residues in order to increase the quantity of heat which is stored in the feed to the still before the flashing operation, and employing carriers other than steam. The first is accomplished by recirculating some of the asphalt through the distillation system, while the second principle is applied by adding to the residuum to be flashed from 50% to 150% of kerosene before this residuum is charged to the system. Steam, however, is also usually introduced into the fractionating tower. The distillation temperature is often as high as 750° F. depending on the properties of the charge but extensive cracking is avoided by minimizing the time during which the oil is kept at this temperature as already mentioned above.

The distillation processes of the above type are now successfully applied for deasphalting petroleum oils from Mid-Continent crudes but their value for deasphalting oils from Pennsylvania crudes has yet to be proved.

### Deasphalting with Clay

Adsorbent clays may be employed not only for improving the color of the solvent refined oils but also for deasphalting purposes. Clays can

\* These processes are described in the "Composite Catalog of Oil Refinery and Natural Gasoline Plant Equipment."<sup>3</sup>



*Courtesy: The Lummus Company*

PLATE IV.—Coubrough Distillation Unit.

be applied either by mixing the finely ground clay with the oil, heating to elevated temperatures, and filtering off the clay (contact method), or by percolating the oil through a relatively long column of comparatively coarse clay at temperatures usually not exceeding 212° F. (percolation method).\*

Either of these two processes is satisfactory for refining solvent treated oils to color specifications provided these oils were deasphalted to a greater or less extent by a preliminary deasphalting operation. However, due to the high cost of the clays used in contact operations their application for reducing the carbon residue, i.e., the asphalt content, of an oil is usually impractical. For this reason, the following discussion is limited to percolation operations.†

The effect of percolation on reduction of carbon residue of lubricating oils can be visualized from the following experimental data of Kauffman,<sup>11</sup> which were obtained by percolating a heavy lubricating oil in naphtha solution. The tests refer to the different oil samples after naphtha was removed by distillation.

TABLE 16—Effect of Percolation on Reduction of Carbon Residue

| Material                | Saybolt<br>Universal Viscosity<br>210° F. | Carbon<br>Residue<br>% Wt. |
|-------------------------|---|----------------------------|
| Original stock          | 156                                       | 2.25                       |
| Stream after yields of: |   |                            |
| 10.0 bbls. of oil       | 87  | 0.027                      |
| 23.0 bbls. of oil       | 95  | 0.115                      |
| 75.0 bbls. of oil       | 125                                       | 0.546                      |
| 148.4 bbls. of oil      | 135                                       | 0.932                      |
| 294.6 bbls. of oil      | 140                                       | 1.49                       |
| 500.4 bbls. of oil      | 140                                       | 1.61                       |
| 589.4 bbls. of oil      | 140                                       | 1.79                       |

This shows that although the clay is quite effective in removing the asphalt when the oil is percolated through very large quantities of clay, it cannot be used economically for this purpose unless the conditions are exceptional.‡

In ordinary refinery practice the solvent refined oils are usually finished by contacting or percolating through clay in order to insure a uniform product of desired specifications. When percolation is resorted to, a small additional reduction in the carbon residue of the already

\* For a more complete discussion see Kalichevsky and Stagner.<sup>1</sup> On the use of contact clays see also Funsten.<sup>6</sup>

† Contacting solvent refined oils with clays at elevated temperatures is specified by Stratford and Moor,<sup>7</sup> and Standard Oil Development Co.<sup>8</sup> Distillation of such oils in presence of clay is recommended by Starr and Edwards,<sup>9</sup> and by Standard Oil Development Co.<sup>10</sup>

‡ The Atlantic Refining Co., for instance, does not employ a deasphalting operation in connection with their nitrobenzene process, but finishes the oils directly with clay.

deasphalted and solvent refined oil might be sometimes expected. Such reduction, however, is greater for oils which have a higher carbon residue when charged to the filters than for oils which are already relatively free from asphalt. Thus in percolating a deasphalted and solvent treated Mid-Continent residuum of 75 Saybolt Universal Seconds at 210° F. and of a 0.2 carbon residue through clay using three to one oil to clay ratio by weight the reduction in the carbon residue of the oil was within the limits of the experimental error. However, when the same oil was deasphalted and solvent refined to a carbon residue of 0.7 the carbon residue of the percolated product was 0.5. This shows that although clay might be used for strictly deasphalting purposes only under exceptional economic conditions, its deasphalting properties may be sometimes employed to an advantage in meeting final specifications for the finished products.

### Deasphalting with Sulfuric Acid

The ability of sulfuric acid to remove asphaltic substances from petroleum oils and to lower their carbon residue is well known,\* which suggests its application as a deasphalting agent in treating solvent refined residual stocks. The effect of sulfuric acid refining on such stocks is shown by the following experimental data, obtained on treating a chlorex extracted Mid-Continent residuum with various quantities of 98% sulfuric acid, followed by neutralization with 3% of adsorbent clay.

TABLE 17—Effect of Sulfuric Acid on Extracted Residuum

|  |      |      |      |      |
|--|------|------|------|------|
| Sulfuric acid (lbs./bbl.)              | 0    | 10   | 20   | 50   |
| Gravity, ° A.P.I.                      | 24.5 | 25.7 | 26.4 | 27.4 |
| Saybolt Universal Viscosity at 210° F. | 143  | 128  | 118  | 107  |
| Viscosity index                        | 91   | 92   | 94   | 95   |
| Color, Lovibond (½" cell)              | >750 | >750 | 325  | 104  |
| Carbon residue, % wt.                  | 2.8  | 1.5  | 0.9  | 0.5  |

Sulfuric acid may be sometimes applied to advantage to oils which were both deasphalted and solvent refined, as indicated by the following data obtained on refining a heavy distillate stock from Mid-Continent crude after extracting it with furfural.<sup>12</sup>

TABLE 18—Effect of Sulfuric Acid on Extracted Distillate

|  | Before<br>Extraction | After Furfural<br>Extraction | After Furfural<br>Extraction and<br>Refining with 5 lbs.<br>98% H <sub>2</sub> SO <sub>4</sub> per bbl. |
|--|----------------------|------------------------------|---|
| Gravity, ° A.P.I.                      | 21.7                 | 26.1                         | 26.4  |
| Saybolt Universal Viscosity at 210° F. | 81                   | 70                           | 70  |
| Viscosity index                        | 65                   | 75                           | 87  |
| Carbon residue                         | 0.73                 | 0.37                         | 0.16  |

\* Details of sulfuric acid refining of lubricating oils are described by Kalichevsky and Stagner.<sup>1</sup>

The effect of sulfuric acid is less pronounced with stocks, which were very thoroughly deasphalted and solvent refined before the acid is applied. This is shown by the following data obtained on refining a heavily Duo-Sol treated Mid-Continent residuum with various quantities of 98% sulfuric acid, followed by clay neutralization.

TABLE 19—Effect of Sulfuric Acid on Duo-Sol Treated Residuum

|  |      |      |      |
|--|------|------|------|
| Sulfuric acid (lbs./bbl.)              | 0    | 10   | 50   |
| Gravity, ° A.P.I.                      | 28.8 | 29.0 | 29.2 |
| Saybolt Universal Viscosity at 210° F. | 64.6 | 64.4 | 62.8 |
| Viscosity index                        | 99   | 100  | 100  |
| Color, Lovibond (1" cell)              | 58   | 30   | 25   |
| Carbon residue, % wt.                  | 0.22 | 0.18 | 0.16 |

The data also show that besides improving the carbon residue of an oil, sulfuric acid refining has a beneficial effect on its color and viscosity index characteristics, although the actual necessity of applying the acid to solvent refined oils from the viewpoint of the refiner can be determined only after studying the individual characteristics of the stocks processed at the plant.\*

### Deasphalting with Metallic Chlorides

Asphaltic substances can be also removed from petroleum oils by a variety of precipitating agents, such as metallic chlorides. Of these agents aluminum chloride is the most active one although ferrous and ferric chlorides, mixtures of aluminum, calcium or mercuric chloride,<sup>14</sup> zinc chloride,<sup>15</sup> finely divided metals in presence of chlorine,<sup>16</sup> etc., have similar effects. These substances are seldom applied in commercial refining due to the necessity of installing special equipment, their relative expensiveness, and the difficulties encountered in disposing of sludges resulting from such operations. In exceptional instances, however, the solvent refined oils may be refined to an advantage with aluminum chloride which is being done by at least one of the large petroleum companies in preparing special grades of lubricating oil stocks.

\* Manley<sup>13</sup> specifies treating furfural refined oil with sulfuric acid and clay.

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## Chapter IX

### Deasphalting with Solvents

The modern methods for removing asphalt from petroleum oils are based on the ability of certain solvents to precipitate the asphaltic substances when such solvents are mixed with the asphalt bearing stocks. The present commercial processes employ for this purpose propane and related hydrocarbon substances, although aliphatic alcohols seem also to present distinct commercial possibilities. These two types of solvents are, therefore, discussed in this chapter. Besides the above solvents a number of other solvents are known which are capable of precipitating at least some of the asphalt. These solvents, however, which are usually of oxygenated type, such as organic esters or ethers, are considerably less effective than liquefied hydrocarbons or alcohols and are, for this reason, of minor importance. Their detailed discussion is, therefore, omitted in this book.

#### Deasphalting with Liquefied Hydrocarbons

The ability of light petroleum distillates to precipitate asphalt from residual stocks has been discussed in Chapter VII, but such distillates do not give the sufficiently sharp separation between the oil and asphalt which is desired in petroleum refining. However, studies along these lines, extended to cover the lighter members of the hydrocarbon series, such as propane, which can be liquefied at ordinary temperatures by applying pressure showed great promise. The use of these liquefied hydrocarbons for precipitating asphalt from mineral oils had been patented by K. Kling of the Polish Institute for Chemical Research "Metan" as early as 1920.<sup>1</sup> He found that methane, ethane, propane and butane might be employed advantageously for this purpose. This is well illustrated by the experimental data of Bray, Swift and Carr,<sup>2</sup> which are presented in Figure 7. The data show that by employing identical conditions of extraction the separation of asphaltic and high molecular weight substances from petroleum oils proceeds to a greater extent as the molecular weight of the solvent becomes lower.

As already pointed out in Chapter VII, solvents which are used for precipitating asphalt are also capable of precipitating high molecular weight hydrocarbons which may not necessarily be of undesirable asphaltic nature. The use of lighter solvents tends to increase the separation of such high molecular weight substances from the oil with

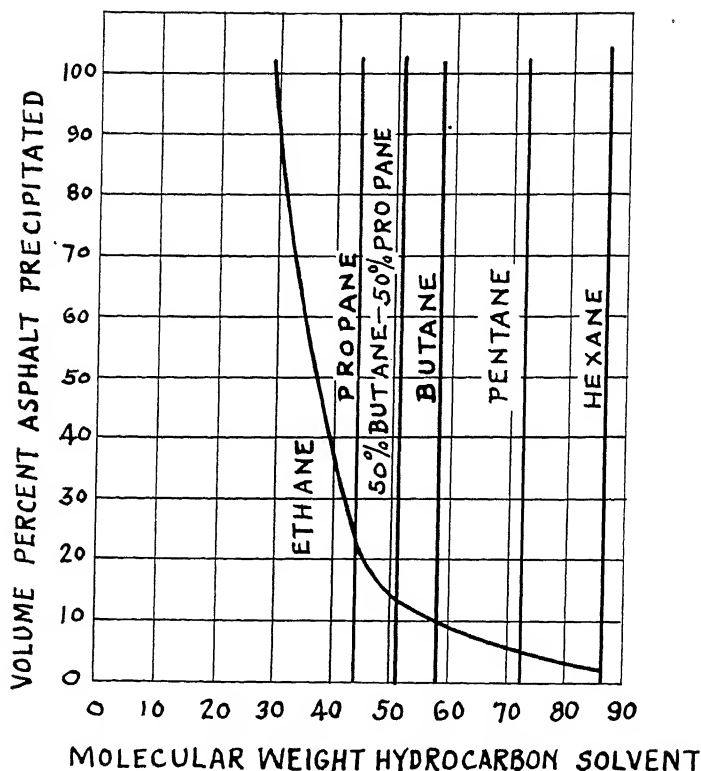


FIGURE 7.—Effect of Molecular Weight of Saturated Hydrocarbon Solvent on Volume Per Cent Asphalt Precipitated from Topped Poso Creek Residuum (10 Volumes Solvent at 80° F.).

the resulting decrease in the yield and viscosity of the recovered product. Experimental work showed, however, that liquefied propane is capable of giving in this respect a better separation between the oily and asphaltic constituents of an oil than other similar substances, as the use of hydrocarbons lighter than propane results in a considerable precipitation of the heavy oil fractions, while the use of heavier hydrocarbons results in an incomplete precipitation of the asphalt. For this reason propane has been chosen as the proper solvent for commercial use and methods of applying it to mineral oils were, therefore, patented by a number of large petroleum companies including the Standard Oil Co. of Indiana, Standard Oil Co. of New Jersey, and the Union Oil Co. of California.<sup>3</sup>

It is also possible to use proper mixtures of liquefied hydrocarbons other than propane and to adjust them so as to obtain the required deasphalting properties. It is likewise possible to use propane in mixtures

with other hydrocarbons such as ethane or butane, etc., as illustrated by the experimental data of Bray, Swift and Carr,<sup>2</sup> presented in Figure 8. These data show that in extracting a residual oil with various propane-ethane and propane-butane mixtures under identical experimental conditions the viscosity of the recovered oil, which is parallel to other properties such as gravity or carbon residue, as well as to the yield, is a direct function of the composition of the solvent mixture. The use of such mixtures, however, in preference to propane is usually less satisfactory on account of their higher vapor pressures in comparison with propane when adjusted to equal deasphalting characteristics.

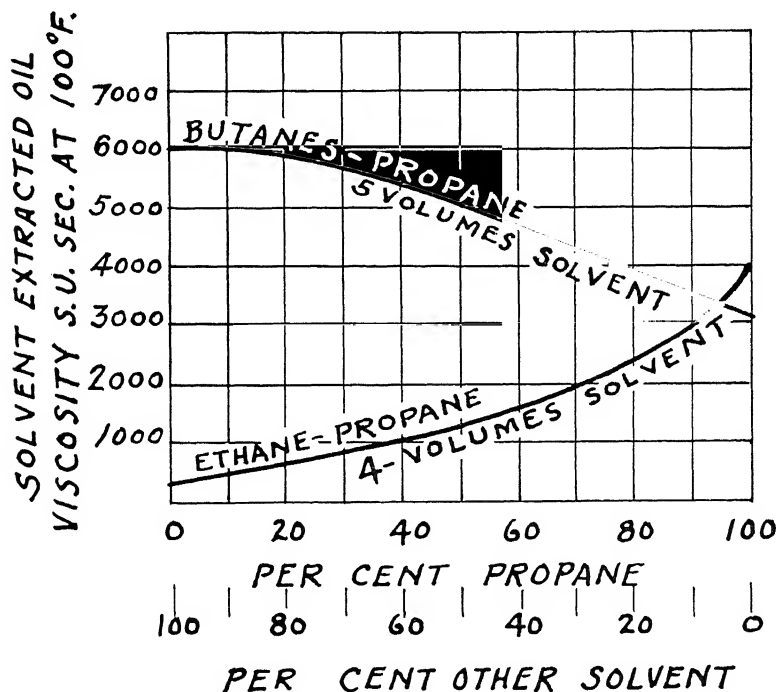


FIGURE 8.—Effect of Proportion of Butanes and Ethane in Propane on Viscosity of Oil Extracted from Poso Creek Residuum at 80° F.

Mixtures of the above type including those of propane with methane and hydrogen were studied also by Godlewicz and Pilat,<sup>4</sup> and many of them are protected by patents.

I. G. Farbenindustrie A.-G.<sup>5</sup> specifies separation of asphaltic bodies from oils by contacting them with liquefied ethane, propane, butane, or ethylene in long tubes under pressure; a British Patent<sup>6</sup> employs propane which, according to the patent, can be replaced with methane, ethane, butane, pentane, hexane, ethylene,

propylene, *iso*-butane, *iso*-pentane, pentylene, hexylene, cyclohexane, or gases and liquids, which are obtained by cracking, destructive hydrogenation or in debutanizing gasoline. Treatment may be done in presence of selective solvents such as phenol, cresol, xylene, cresylic acid, nitro-benzol, aniline, crotonaldehyde, levulinic acid, pyridine, benzyl alcohol, nitro-toluene, furfural, or ethylene-glycol monoethyl ether. Bray and Swift,<sup>7</sup> and Standard Oil Development Co.,<sup>8</sup> specify the mixture of ethane and propane. Bray<sup>9</sup> claims that by utilizing a gaseous hydrocarbon solvent the major portion of which consists of hydrocarbons of less than three carbon atoms per molecule, asphalt is separated which has a lower carbene content and a higher solubility in light naphtha than an asphalt of the same melting point produced by distillation. N. V. Bataafsche Petroleum Maatschappij<sup>10</sup> divides mineral oils into fractions of different molecular weight by treatment in stages with methane, ethane, propane, butane, pentane, ethylene, acetylene, chloroethane, di-chlor-di-fluor methane, carbon dioxide, ammonia, methyl ether, methyl-ethyl ether or  $\text{NH}(\text{CH}_3)_2$ . Bray<sup>11</sup> refines the oil with liquid ethane after a preliminary treatment with liquid propane. Whitley and Beiswenger<sup>12</sup> deasphalt mineral oils with from 3 to 15 volumes of a liquefied hydrocarbon mixture containing hydrocarbons with 1 to 5 carbon atoms; etc.

Their work showed the possibility of employing such combinations for separating petroleum oils into fractions of different physical and chemical characteristics besides the precipitation of asphaltic substances. Thus after separating asphalt with a properly adjusted mixture of propane and butane, addition of methane caused separation of the remaining oil into two layers. By increasing the pressure of methane from 30 atm. to 130 atm. only a few percent of a very light yellow colored oil remained in the methane saturated solution. The two layers differed in viscosity, viscosity index and viscosity-gravity constant although their specific gravity was similar. While with methane the first signs of turbidity with a deasphalted Venezuela residual oil occurred at a pressure of 18 atm. by replacing methane with carbon dioxide and by employing the same propane-butane mixture the first signs of turbidity were observed at 15 atm. pressure, with nitrogen at 28 atm. and with hydrogen at above 86 atm. These experiments seem further to bring out the dual action of light hydrocarbons on mineral oils whereby they are capable of effecting separations into fractions both by precipitating the colloiddally suspended substances and by actual solubility effects.

As already mentioned, certain quantities of asphalt can also be separated from the oil with petroleum ether or somewhat heavier petroleum fractions, although the results are less satisfactory than with propane or similar substances. Attempts are, therefore, recorded to separate asphalt from crude mineral oils by counter-current circulation of light gasoline in a continuous column,<sup>13</sup> or by employing solutions of propane in benzol,<sup>14</sup> which are claimed to be particularly suitable for refining oxidized asphalt by separating it into an oil fraction and a bituminous fraction substantially free from oil.

Due to the commercial importance of the propane process most of the available information concerns application of this particular substance to the refining of mineral oils. Recent developments along these lines are summarized by Wilson, Keith and Haylett,<sup>15</sup> who point out

the following characteristic properties of propane when applied as a solvent for mineral oils within certain temperature ranges:

- (1) The higher the temperature, the less is the solubility of oil in propane,
- (2) The more propane is added to an asphalt bearing oil, the less asphalt is dissolved,
- (3) Pressure has a large effect on solubility,
- (4) Compressed propane gas will, at certain temperatures, dissolve more oil than liquid propane at slightly lower temperatures and pressures.

The above can be explained by assuming that two independent phenomena take place when oil is mixed with propane: colloidal precipitation of asphalt particles and true solubility phenomena with respect to the heavy petroleum constituents other than asphalt. The observation that gaseous propane dissolves under certain conditions more oil than liquid propane is in accordance with the principle of retrograde condensation. Within a certain temperature region increase in pressure has a decided effect on the solubility relationships for complex mixtures of liquids and gases. For a constant temperature and pressure below a certain minimum the mixture is in a homogenous vapor state. Further increase in pressure results in the separation of a liquid phase which is richer in the high boiling constituents than the vapor phase co-existing with it. As the pressure is increased the volume of the liquid or more dense phase increases at first until it reaches a maximum then starts to decrease, *i.e.*, the liquid phase dissolves in the compressed vapor, until it is completely dissolved and the mixture again becomes completely homogenous. This behavior is, in all probability, characteristic of propane-oil mixtures in the temperature region immediately above the critical temperature of pure propane. It has been also previously observed in the study of cracking phenomena by E. Peck of the Standard Oil Development Co.

An interesting diagrammatical representation of the behavior of propane and mineral oil mixtures at different experimental conditions on triangular diagrams has been made by Wilson, Keith, and Haylett,<sup>16</sup> and is shown in Figure 9. These "idealized" diagrams are used, however, only in a qualitative way as, with the exception of propane, the two other so-called fixed components, oil and asphalt, cannot be considered as pure substances. For these reasons, the definition of oil and asphalt varies with the experimental conditions, asphalt being considered those components which are rejected from the propane solution, and oil, those constituents which are soluble in propane under the given temperature and pressure conditions. Therefore, the greater the quantity of the asphalt rejected, the lower is the viscosity of the oil and its carbon residue, and the lower is the "melting point" of the precipitated asphalt.

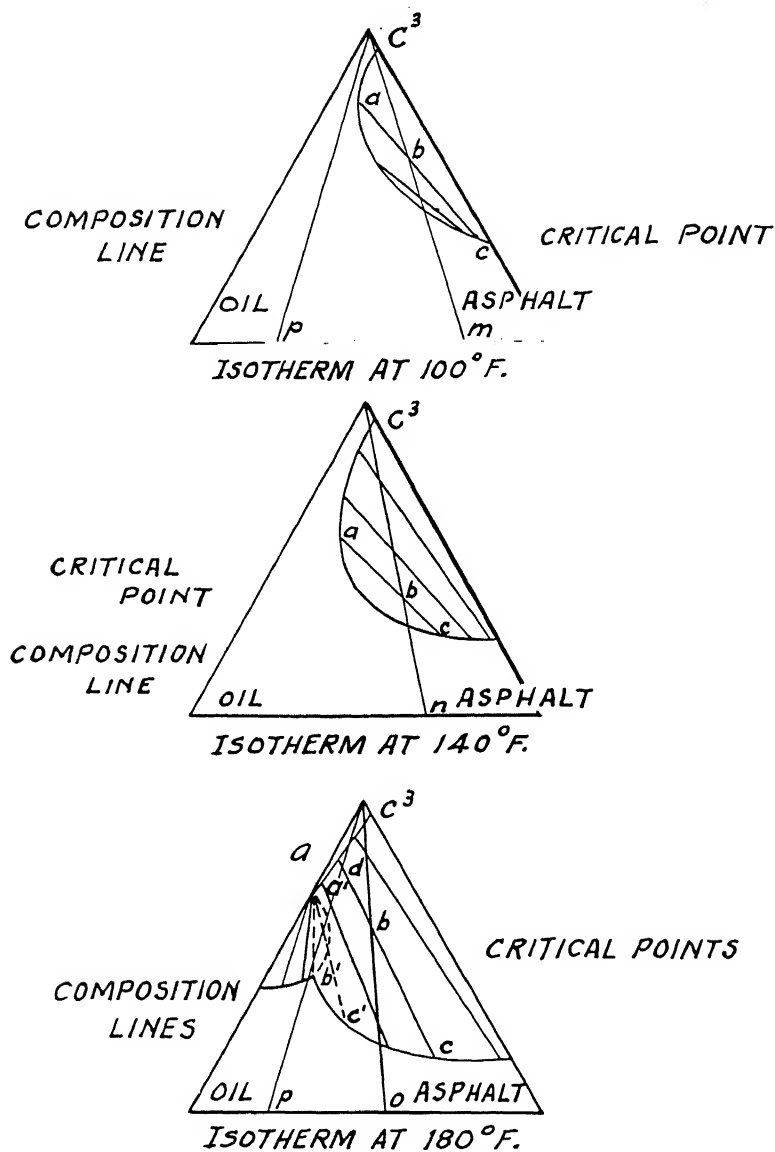


FIGURE 9.—Idealized Diagram for the System Propane-Oil-Asphalt.

Asphalt has strictly no melting point and the amount of heat necessary for its liquefaction is dependent upon the consumption of heat caused by the specific heat of asphalt.<sup>17, 18</sup> For this reason, whenever the reference is made to the "melting point" of asphalt it simply implies the readings of one of the several arbitrary tests which are accepted for measuring this "property" of asphalt, *i.e.*, the temperature at which the fluidity of asphalt falls beyond a certain minimum.

As already mentioned in the previous chapters, all of the hydrocarbon solvents which were discussed above are also dewaxing solvents. Thus, they are capable of precipitating both asphalt and wax and a sharp separation between these two substances is therefore difficult. Unless the asphalt is first separated at higher temperatures, all of it will be precipitated with the wax.

I. G. Farbenindustrie A.-G.,<sup>19, 20</sup> Bray,<sup>21, 22, 23</sup> and other patents, cover combined dewaxing and deasphalting operations. Alco Products Inc.<sup>24</sup> simultaneously separate wax and asphalt by treating with propane by first heating the mixture and precipitating the asphalt and then, without removing the precipitate, by passing the mixture into a cooling zone and depositing the wax around the asphalt particles: Aldridge and Hopper<sup>25</sup> precipitate "hard" and "soft" asphalts with liquefied hydrocarbons in two stages.

Such contaminations can be reduced, however, to a reasonable minimum, provided the conditions employed for separating these substances are strictly controlled. Similar conditions are encountered with other deasphalting solvents, which are also capable of acting as dewaxing agents.

In commercial installations, deasphalting with propane is accomplished by mixing residual oil with propane at a predetermined temperature and under pressure, settling the precipitated asphalt, and removing it from the oil.

Attempts are being made to increase the settling rate and improve the separation of the asphalt by passing the mixture through an electric field of high tension,<sup>26</sup> etc., but none of such accelerated methods are apparently in commercial use.

The ratios of propane to oil are frequently as high as 9 to 1 in order to insure satisfactory precipitation while the temperatures employed are about 120-130° F. but may be higher or lower depending on the properties of the stock to be deasphalted. Large dilutions are required also for reducing the losses as the separation of precipitate from the liquid layer is usually not very definite. For this same reason propane is applied counter-currently, *i.e.*, the precipitate from the previous settling operation is washed with fresh propane which is then applied to a fresh oil charge. The precipitated asphalt is usually sufficiently fluid to permit its removal by pumping, while the counter-current washing of the precipitate reduces the quantity of oil rejected with asphalt to a minimum. After removing the asphalt the oil may be chilled for separating the wax as described in the chapter on dewaxing.

In general, propane is used as a dewaxing agent at temperatures between -44° F. and +70° F., and as a precipitant for asphalt at above

70° F. As already mentioned, above its critical temperature and at 1000 lbs. per sq. in. pressure propane is more dense than in liquid state at 212° F. and its saturation pressure and has a higher solvent power for oil.\*

### Deasphalting with Aliphatic Alcohols

After light hydrocarbons, aliphatic alcohols appear to be the most promising ones among the deasphalting solvents.<sup>28</sup> Like propane they also precipitate some of the heavy hydrocarbon fractions present in the oil and can be used as dewaxing solvents, as discussed in Chapter V. Alcohols differ from propane, however, in requiring lower temperatures for the best display of their deasphalting characteristics although their behavior close to or above the critical temperatures has not been investigated. Due to the low deasphalting temperatures it is difficult to make a sharp separation between wax and asphalt as the higher melting point waxes are usually removed with the main bulk of asphalt while the major portion of the wax contains some of the soft asphalt. In this respect propane is superior to alcohols which are particularly adaptable to products which contain little wax and large quantities of harder types of asphalt.

Considering the normal aliphatic alcohols, it can be observed that under identical treating conditions the yield of oil and its viscosity show a gradual increase when the molecular weight of the alcohol used in extractions is gradually increased. This is illustrated by the following experimental data obtained in extracting a Mid-Continent residuum of 100 Saybolt Universal seconds at 210° F., and a 3.1 carbon residue, with five volumes of alcohols at 35° F.

TABLE 20—Extraction with Aliphatic Alcohols

| Alcohol      | Yield<br>% Volume | Carbon<br>Residue | Saybolt Universal<br>Viscosity at 210° F. |
|--------------|-------------------|-------------------|---|
| Ethyl* ..... | 45                | 2.1               | 54.1                                      |
| Butyl .....  | 71                | 1.9               | 85  |
| Amyl .....   | 77                | 1.7               | 87  |
| Hexyl .....  | 89                | 2.6               | 97  |
| Octyl .....  | 100               | 3.1               | 100                                       |

\* This alcohol was applied at 275° F., as, at 35° F., it is practically immiscible with oil.

The data show that for a given oil yield the quantity of the asphalt precipitated from the residuum, as indicated by the decrease in the carbon residue of the extracted oil, reaches its maximum with butyl and amyl alcohols. The higher alcohols also possess, however, some deasphalting properties, but the low temperatures required for displaying them are such that the viscosity of the alcohol-oil mixtures is usually too high to

\* For detailed information concerning commercial deasphalting processes, see Bahlke, Thiele, Adams, and Ginsberg.<sup>27</sup>

permit an effective separation of the precipitated fractions, unless filter-aids and pressure filtration are resorted to.

Another modifying factor is the isomeric structure of the alcohols. Thus, under similar treating conditions, refining of a residual oil from German crude with 5 volumes of alcohols at 20° F., gave the results listed in the following table.

TABLE 21—Effect of Isomeric Structure of Extracting Alcohols

| Oil before<br>Alcohol<br>extraction   | Yield<br>%<br>Volume<br>100 | Carbon<br>Residue<br>6.6 | Saybolt<br>Universal<br>Seconds<br>210° F.<br>232 | Pour<br>Point<br>° F.<br>>100 |
|---|-----------------------------|--------------------------|---|-------------------------------|
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2\text{OH} \end{array}$ | 73                          | 2.9                      | 101   | 15                            |
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2\text{OH} \end{array}$ | 67                          | 2.7                      | 97  | 10                            |
| $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}_2-\text{COH} \\   \\ \text{CH}_3 \end{array}$ | 89                          | 4.3                      | 136   | 30                            |
| $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHOH}-\text{CH}_3$   | 77                          | 2.9                      | 104   | 20                            |
| $\text{CH}_3-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{CH}_3$   | 82                          | 3.1                      | 109   | 20                            |

It is, evidently, also possible to modify the action of alcohols by employing their various mixtures, which act in a manner similar to the pure alcohols.

The effect in single-stage extractions of the extraction temperature and the alcohol to oil ratio employed on the yield and carbon residue of the resulting product is shown in Figure 10. The experimental data refer to fusel oil extractions of a Mid-Continent residuum of 144 Saybolt Universal seconds at 210° F. having a 90° F. pour test and a carbon residue of 3.5.

Addition to alcohols of various substances, such as acetates, ketones, hydrocarbons, etc. likewise modifies their deasphalting characteristics. Frequently, such dilutions might be helpful in adjusting the alcohol-oil mixtures for exhibiting their best deasphalting and dewaxing characteristics by improving the solvent power of alcohols at low temperatures required for dewaxing. An oil can, for instance, be deasphalted with alcohols at somewhat higher temperatures and then diluted with additional quantities of such solvents and dewaxed at those lower temperatures at which the alcohols alone tend to precipitate some of the oil.

The presence of water has a marked effect on the extraction efficiency of alcohols. This is shown by the results in Table 22, obtained in extracting a Mid-Continent residuum of 100 Saybolt Universal seconds, 3.5 carbon

residue and 90° F. pour test, with anhydrous amyl alcohol, and with the same alcohol containing 5% water; 5 volumes of alcohol at 20° F. were employed.

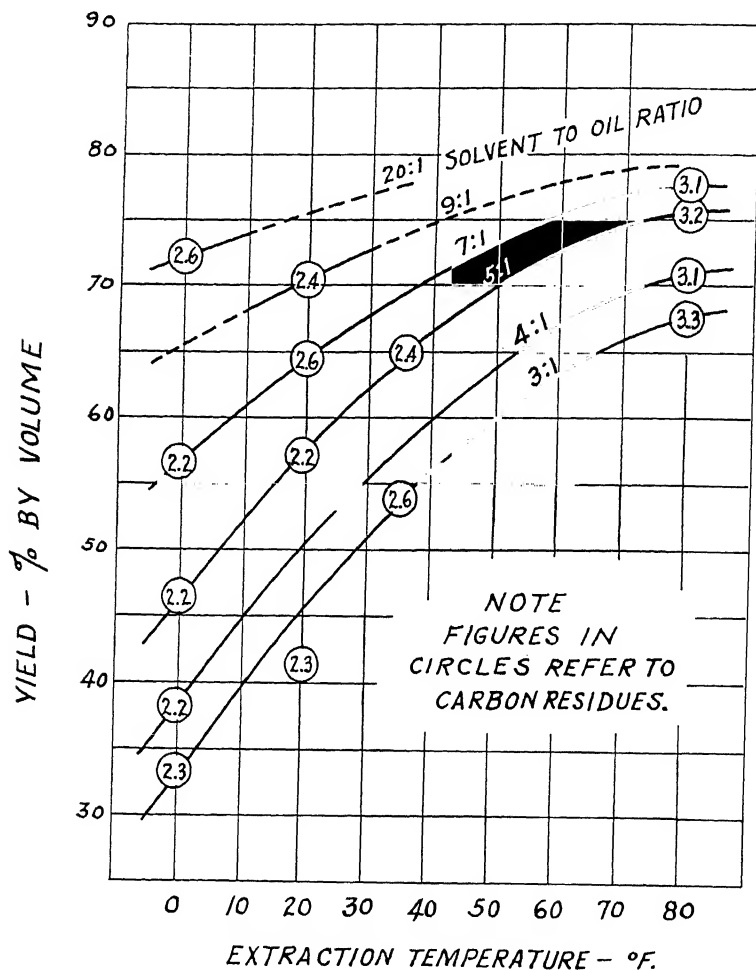


FIGURE 10.—Effect of Treating Conditions on the Yield and Carbon Residue of a Mid-Continent Residuum (Batch Extractions with Refined Fusel Oil).

The yields referred to in the above tables and in Figure 10 were obtained by single batch extractions. They can usually be increased by employing multi-stage countercurrent and recycling operations, but only under exceptionally favorable conditions can they be made equal to those

TABLE 22—Effect of Presence of Water on Extraction Efficiency

|                                   | Extracted Oil          |                             |
|-----------------------------------|------------------------|-----------------------------|
|                                   | Anhydrous Amyl Alcohol | Alcohol Containing 5% Water |
| Yield, % volume                   | 77                     | 52                          |
| Pour, °F.                         | 20                     | 20                          |
| Carbon residue                    | 1.4                    | 0.9                         |
| Saybolt Universal Seconds 210° F. | 70                     | 62                          |

obtained with propane for an equal reduction in the carbon residue content of the oil. In general, alcohols are applied with best results on oils containing large proportions of hard asphalts which are removed with relative ease, but they become progressively less effective deasphalting agents after the carbon residue of an oil is reduced below a certain minimum. Since no expensive high pressure installations are needed and the fire hazard involved in handling alcohols as compared with propane is relatively small, the alcohols may be of value as deasphalting agents in refining some specific refinery products. For this reason, it might be expected that they will gradually become of some commercial importance in refining residual stocks from certain types of crudes.

There are recorded for commercial utilization of aliphatic alcohols as deasphalting agents numerous patent applications which frequently specify the use of aqueous alcohols or addition of water during the extraction process for altering the solubility characteristics of the solvent mixtures.

Werschen-Weissenfeller Braunkohlen A.-G.<sup>30</sup> treats petroleum residual oils containing wax and asphalt with fusel oil or similar mixtures, adds to the mixture from 0.5% to 5% of water, and after chilling to the desired temperature, separates the precipitated asphalt and wax by decantation; N. V. de Bataafsche Petroleum Maatschappij<sup>30</sup> uses a mixture of a secondary or tertiary aliphatic alcohol and a polar substance, such as water, lower aliphatic alcohols or ketones, etc. Widdecke<sup>28</sup> describes a rather elaborated scheme for refining oils with aqueous amyl alcohol for removal of wax and asphalt in which the water content of the alcohol is varied in the course of the extraction. Krauch, Pier, and Eisenhut,<sup>31</sup> employ a mixture of methyl alcohol and a hydroaromatic hydrocarbon such as cyclohexane for removing resinous and asphaltic substances; etc.

The selective solvent action of methyl, ethyl, propyl, butyl and amyl alcohols on asphalts from different origins has been also investigated.<sup>32</sup> Propyl alcohol is, apparently, slightly superior in this respect to other alcohols, although, in general, the physical characteristics, ash content and elementary analysis of the separated fractions showed only minor differences.

As already mentioned the deasphalting solvents are also capable of separating the oil into fractions of somewhat different physical and chemical characteristics. This has been recognized for a number of years as alcohols were recommended for refining the light petroleum fractions at the early beginning of the petroleum industry.\*

\* Tyler<sup>33</sup> already employed fusel oil for refining kerosene.

Similar attempts are recently recorded for utilizing these properties of alcohols in refining lubricating oil fractions<sup>34</sup> but, apparently, this has not yet found commercial applications.

Besides light petroleum hydrocarbons and aliphatic alcohols, a variety of other substances are likewise capable of exhibiting some deasphalting characteristics. These substances are usually of the oxygenated type, such as esters, ethers, or ketones, but their deasphalting action, in most instances, is not sufficiently strong to warrant their detailed description. The effect of selective refining solvents on the reduction of the asphalt content of oils is discussed in the subsequent chapters. These selective solvents are, however, of the type of asphalt solvents rather than asphalt anti-solvents as have been just discussed.

### Deasphalting Plants

Previous discussion showed that the propane process is the only commercial solvent deasphalting process in existence. The following tabulation gives the capacities of the propane deasphalting and deresining plants and their distribution between various oil companies.

TABLE 23—Propane Deasphalting and Deresining Plants

| Company, Location and Year of Construction         | Charging Capacity<br>Bbls./Day   |
|--|--|
| Shell Petroleum Co., Wood River, Ill., 1935.....   | 3,300 (Deasphalting followed by dewaxing in propane solution).                     |
| Texas Co., Port Arthur, Tex., 1936.....            | 1,960 (Deasphalting and deresining).   |
| Standard Oil Co. of Ind., Whiting, Ind., 1936..... | 1,200 (Propane deasphalting combined with acid treating in propane solution).      |
| Kendall Refining Co., Bradford, Pa., 1936.....     | 900 (Deresining combined with propane dewaxing).                                   |
| Humble Oil Refining Co., Baytown, Texas., constr.  | 4,800 (Deasphalting combined with dewaxing and acid treating in propane solution). |
| Standard Oil Co. of La., Baton Rouge, La., constr. | 2,100 (Deasphalting).  |
| Union Oil Co. of Cal., Oleum, Cal., 1934.....      | 2,000 (Deasphalting).  |
| Bradford Penn. Refining Co., Warren, Pa., 1936...  | 250 (Deresining combined with propane dewaxing).                                   |
| Total.....   | 16,510   |

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## Chapter X

### General Principles of Solvent Refining Processes

The conventional sulfuric acid methods of oil refining are based on the removal of the undesirable oil constituents by a simultaneous chemical and physical action of this reagent. Variations in treating temperature, method of applying the acid, time of contact, acidity of treating acid, etc., permit us within certain limits to regulate the selective action of the acid towards the individual oil constituents, which explains the rather considerable flexibility of the method when applied to the manufacture of a variety of petroleum products of different characteristics.\* As it is impossible, however, to eliminate completely the chemical effect of sulfuric acid on petroleum oils, a series of new reaction products are always formed in the course of refining, such as sulfonated compounds, polymerized or condensed compounds, etc., some of which are left in the refined oil and may have an unfavorable effect on its properties. Considerable difficulty is also encountered in the disposal of sulfuric acid sludge which can be profitably utilized only in a few isolated instances.

#### Early Investigations of Refining Solvents

The possibility of removing undesirable constituents from petroleum oils by purely physical action of the solvents offered for these reasons attractive possibilities since the very beginning of the petroleum industry. The first attempts in this direction should be, apparently, ascribed to A. M. Butlerov who applied solvents to petroleum oils as early as 1870.<sup>2</sup> Similar investigations were carried out at later dates by Aisinman,<sup>3</sup> Zaloziecki,<sup>4</sup> and Charitschkoff,<sup>5</sup> but it was not until the commercially successful work of Edeleanu with liquid sulfur dioxide that solvent refining proved to be of practical as well as of theoretical importance.<sup>6†</sup>

This work of Edeleanu showed that liquid sulfur dioxide can be profitably utilized for refining kerosene fractions of petroleum and that in addition to considerable savings none of the oil was lost to sludge. The extracted fractions proved, of themselves, to be valuable by-products which could be utilized as solvents or as sources of aromatic compounds, etc., thus permitting a full utilization of the raw distillates never achieved before.

\* For a complete discussion see Kalichevsky and Stagner.<sup>1</sup>

† For further discussion of the process as applied to refining of light petroleum distillates see Kalichevsky and Stagner.<sup>1</sup>

The solvent refining methods applied to kerosenes, were soon extended to the field of lubricating oils, which presented, however, some added problems that could not be satisfactorily solved before the effect of the deasphalting processes was clearly understood. Moreover, only a few years ago, relatively speaking, such important characteristics of lubricating oils as viscosity-temperature relationships or oxidation stability were not yet well realized, and improvement in color was usually considered as the main object in refining such type of products. For these reasons, the necessity of applying solvents to lubricating oils in order to achieve such improvements at the minimum cost of refining assumed its practical significance only with the introduction of high specification standards for the refined oils.

The first extensive investigation of the effect of different solvents on the improvement of lubricating oil properties was published by Ferris, Birkhimer and Henderson,<sup>7</sup> who investigated the relative abilities of 110 solvents to separate lubricating oil stocks into two dissimilar fractions. The fraction containing the largest proportion of the solvents and corresponding to the extract phase was referred to as "naphthenic" because it approached more or less closely in some of its properties the highly naphthenic base oils of the Gulf Coast type. The fraction containing the largest proportion of the oil and corresponding to the raffinate phase was referred to as "paraffinic" because it approached in some of its characteristics lubricating oils from highly paraffinic crudes, such as Pennsylvania crudes. The quantity of solvent used based on the volume of the lubricating stock employed ranged from 50% to 500%. The viscosity-gravity constant was accepted in the laboratory experiments as an index of the degree of separation obtained between the two phases by means of solvents. Although space does not permit a detailed discussion of this work, it should be added that in all of the experiments in which separation occurred, it was due more to the greater solubility of the "naphthenic" type of oil components than to that of the "paraffinic" type of components in such solvents.

Although the above publication was the first of its type to appear in the literature, many of the larger petroleum companies were already carrying out such investigations. As a result, at the time when the industry was ready to abandon the old sulfuric acid treating methods used for manufacturing the major portion of the lubricating oil products, several competing solvent refining processes were placed on the market and were successfully applied at various refineries.

### **Solvent Refining Methods**

Solvent refining is based on the differences in the solubility of the various types of hydrocarbons present in petroleum in the solvent. Several methods can be used, however, in applying the solvent to the oil. These may be classified as follows:

1. Single batch extraction when the solvent is applied to the oil in a single portion.
2. Multiple batch extraction when the solvent is applied to the oil in several portions each portion consisting of the fresh solvent.
3. Counter-current extraction when the solvent partially spent in contacting with a semi-refined product is utilized for extracting a product containing still larger proportions of impurities, while the fresh solvent is used on the oil leaving the extraction system. Such counter-current extractions may be performed either in multiple batch operations or in counter-flow towers.

### Theoretical Analysis of Solvent Refining

Assuming that the oil consists of two distinct components, one of which is immiscible with the solvent while the other, or the impurities, is soluble both in solvent and in oil, the equations given below, were derived by Nash,<sup>8</sup> and are of value in making theoretical comparisons between the three methods of applying solvents as described above.

Other theoretical derivations of similar type, some of which employ graphical methods, for calculating efficiencies of extraction processes were developed by Hunter and Nash,<sup>9, 10</sup> Evans,<sup>11</sup> Kurtz,<sup>12</sup> Thiele,<sup>13</sup> Varteressian and Fenske,<sup>14</sup> Underwood,<sup>15</sup> and Francis.<sup>16</sup> Thompson<sup>17</sup> explains the use of triangular diagrams as applied to solvent extraction.

1. Single batch extractions.

$$\frac{\frac{y_1}{P}}{y_0 - y_1} = K, \text{ or}$$

$$W$$

$$y_1 = y_0 \left( \frac{KP}{KP + W} \right)$$

2. Multiple batch extractions.

$$y_n = y_0 \left( \frac{KP}{KP + W} \right)^n$$

3. Counter-current extractions.

$$y_n = \frac{x_0 C (C^n - 1) + y_0 C^n (C - 1)}{C - 1 + C (C^n - 1)}$$

In these equations the following symbols are used:

$K$  = distribution coefficient =  $\frac{C_1}{C_2}$ , where  $C_1$  and  $C_2$  are concentrations of impurities in the oil and solvent phase respectively,  
 $y_0$  = concentration of impurities in oil before extraction,  
 $y_n$  = concentration of impurities in oil after  $n$ th extraction,  
 $P$  = volume of oil free of impurities,

$W$  = volume of solvent free of impurities,

$$C = \frac{KP}{W}.$$

These equations show that single batch extraction is the least efficient and that counter-current extraction is the most efficient. Counter-flow towers can be regarded as counter-current batch extractors considering a given height of the column to be equivalent to one ideal extraction stage.

Attempts are also made to draw parallels between solvent extraction and distillation processes but the value of such comparisons appears to be open to question.

These theoretical considerations, although of considerable value in understanding the basic principles of extraction, lose much of their significance when applied to practical petroleum problems. The oil cannot be considered as consisting of two distinctly different components and, therefore, the quantity of the impurities removed from the oil as well as their quality depends entirely on the severity of extraction. The distribution coefficient is, for this reason, also a variable and, moreover, changes with each extraction step as the solvent becomes increasingly more saturated with the impurities removed from the oil. Likewise, the oil and the solvent are not mutually insoluble and the oil phase always contains some of the solvent and the solvent phase some of the desirable oil fractions. Solvent extraction, therefore, continues to be dependent on the actual results of experimenting with the particular solvent and oil in which the refinery is interested. Further discussion of the principles involved in extracting oils with solvents in commercial plants is given in subsequent chapters.

### Solvent Analysis

In practice, however, it is frequently necessary to obtain quick information about the available yield of oils of various qualities from a given charging stock, or the quantity of satisfactory oil rejected into extract, or the approximate composition of the refined product. Such approximations can be obtained by the method of Bray, Pollock, and Merrill,<sup>18</sup> which is a modification of the "Allbreaction" recommended by Lee,<sup>19</sup> for identification of various crudes by plotting the gravities of residues obtained from a given crude in a series of acid treatments.

According to this method the oil is repeatedly extracted by employing a constant volume of fresh solvent at temperatures required to maintain a substantially constant concentration of oil in the extract phase. The resulting extracts are analyzed for gravity, refractive index, viscosity or some other significant property and the results are plotted against the total amount of material removed up to the mid-point of the cut in question. An example of such curves is given in Figure 11, where Bray, Pollock and Merrill show the differences obtained in extracting an oil in the above described manner when the increments of the extracted oil fractions are small (Curve 1) or large (Curve 2). These results are compared with

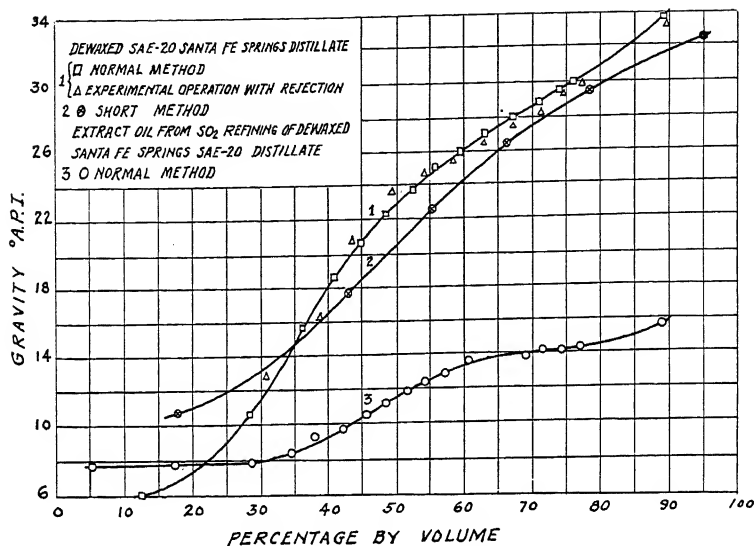


FIGURE 11.—Solvent Fractionation of Lubricating Oils.

those obtained by extracting the oil in a normal manner (Curve 3) which does not permit the sharp differentiation between the various oil constituents as obtained by the proposed method. However, countercurrent extractions will better results forecast by this analytical multiple batch extraction method.

### Substances Removed in Solvent Refining

Analyses of the above type were employed for investigating the selectivity exercised by solvents in removing various constituents from petroleum oils. In these investigations acetone was employed as the selective solvent and the oils were extracted by the multi-stage method applying each time a fresh portion of the solvent.<sup>23</sup>

As with all selective solvents the solvent power of acetone decreases with the increase in the viscosity of the oil, and while acetone is miscible with the light petroleum fractions it has but slight solvent power for the high molecular weight hydrocarbons.<sup>20</sup> Acetone has been generally recommended for dissolving shale and lignite oils from paraffin wax, for separating tarry matter from lubricating oils,<sup>21</sup> for removing from lubricating oils the constituents which resinify on heating,<sup>22</sup> etc.

Relationships between the physical properties and the chemical constitution of lubricating oil fractions and the effect of solvent refining on these properties were investigated by Mair and Willingham,<sup>24</sup> and by Fuchs and Anderson.<sup>25</sup> See also Waterman, Kruijff, Schönlaue, and Tulleners.<sup>26</sup>

These investigations indicated that selective solvents are removing from oils compounds of aromatic type and that subsequent solvent extractions remove compounds of progressively lower aromaticity leaving in the raffinate substances of progressively higher paraffinicity. However,

solvents have also a certain selective action towards the paraffinic type of hydrocarbons of lower molecular weights, which, in some instances, may be more soluble in the solvent than the aromatic compounds of higher molecular weight. This is substantiated by the observation that in the multi-stage extractions mentioned above the plot of the amount of the oil extracted against some of the physical properties of the extracted fractions, such as gravity, may show an inversion.

When the oil is separated into fractions by means of solvents the raffinate phase has a higher API gravity, a higher viscosity index, a lower viscosity-gravity constant, a lower carbon residue, a lower acidity and a lighter color than the charging stock and, particularly, than the extract phase. The boiling point range and the flash and fire points undergo comparatively minor changes, if any. In comparing efficiencies of extraction by the various methods it is frequently customary to draw conclusions on the basis of the change of one constant only. Although this may often be permissible, it should be noted that identical products are obtained only when all of such constants are in complete agreement, as otherwise the products cannot be considered as strictly comparable and the value of the resulting conclusions is, therefore, greatly minimized.

### **Requirements of an Ideal Solvent**

An ideal solvent for extracting oils should possess the following properties:

1. The solvent should be capable of extracting from petroleum oils the undesirable constituents so as to yield marketable products equal or superior to those obtained by other refining methods.

2. The solubility of the solvent in the oil layer should be low, while that of the impurities in the solvent must be high.

3. The solvent should be able to display its best solvent power at temperatures which do not require application of excessive quantities of heat or refrigeration, and at which the oil is sufficiently fluid to insure a good contact.

4. The specific gravity of the solvent should be relatively high and interfacial tension low in order to obtain quick and complete separation into two liquid phases.

5. The freezing point of the solvent should be low in order to avoid complications in handling in cold weather.

6. The solvent must be stable and have no appreciable chemical action on the oil at temperatures encountered in refining or in separating the solvent from the oil.

7. The boiling point of the solvent must be sufficiently low to insure its easy separation from the oil by distillation. It is also desirable that its vapor pressure at the extraction temperatures should not be exceptionally high in order to avoid the use of pressure equipment.

8. The solvent must be available in large quantities and at low cost.
9. The solvent should not exhibit exceptional corrosive properties that would require the use of expensive corrosion resistant materials.
10. The solvent should not be of poisonous or of explosive nature in order to eliminate the danger of handling it at the plant.
11. The quantity of solvent required for extracting the oil must not be excessive so as to insure a reasonable throughput in a plant of normal size.

### Solvent Refining Processes

Although few, if any, of the commercial solvents conform to all of the above requirements, it is nevertheless desirable that they approach them as closely as possible in order to withstand the present market competition.

TABLE 24—Charging Capacity of Solvent-

| Process                               | January 1930    |                  |                             | January 1933    |                  |                             | January 1934    |                  |                             |
|---------------------------------------|-----------------|------------------|-----------------------------|-----------------|------------------|-----------------------------|-----------------|------------------|-----------------------------|
|                                       | Barrels Per Day | Total (Per Cent) | Present Capacity (Per Cent) | Barrels Per Day | Total (Per Cent) | Present Capacity (Per Cent) | Barrels Per Day | Total (Per Cent) | Present Capacity (Per Cent) |
| <i>Plants in the</i>                  |                 |                  |                             |                 |                  |                             |                 |                  |                             |
| Duo-Sol .....                         | ....            | ....             | ....                        | ....            | ....             | ....                        | 1,600           | 47.06            | 11.35                       |
| Furfural .....                        | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Phenol .....                          | ....            | ....             | ....                        | 800             | 100.00           | 13.01                       | 1,800           | 52.94            | 29.27                       |
| Chlorex .....                         | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Sulfur-dioxide-benzol* .....          | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Nitrobenzene .....                    | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Nitrobenzene-sulfuric acid.....       | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Total .....                           | ....            | ....             | ....                        | 800             | 100.00           | 1.58                        | 3,400           | 100.00           | 6.72                        |
| <i>Plants in Europe</i>               |                 |                  |                             |                 |                  |                             |                 |                  |                             |
| Duo-Sol .....                         | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Furfural .....                        | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Phenol .....                          | 2,000           | 100.00           | 34.48                       | 2,000           | 100.00           | 34.48                       | 5,500           | 100.00           | 94.83                       |
| Sulfur-dioxide-benzol* .....          | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Total .....                           | 2,000           | 100.00           | 9.62                        | 2,000           | 100.00           | 9.62                        | 5,500           | 100.00           | 26.46                       |
| <i>Plants in</i>                      |                 |                  |                             |                 |                  |                             |                 |                  |                             |
| Duo-Sol .....                         | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Furfural .....                        | ....            | ....             | ....                        | ....            | ....             | ....                        | 1,600           | 17.98            | 8.66                        |
| Phenol .....                          | 2,000           | 100.00           | 12.27                       | 2,000           | 71.43            | 12.27                       | 5,500           | 61.80            | 33.74                       |
| Chlorex .....                         | ....            | ....             | ....                        | 800             | 28.57            | 13.01                       | 1,800           | 20.22            | 29.27                       |
| Sulfur-dioxide-benzol* .....          | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Nitrobenzene .....                    | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Nitrobenzene-sulfuric acid.....       | ....            | ....             | ....                        | ....            | ....             | ....                        | ....            | ....             | ....                        |
| Total .....                           | 2,000           | 100.00           | 2.88                        | 2,800           | 100.00           | 4.04                        | 8,900           | 100.00           | 12.83                       |
| <i>Comparison of Plant Capacities</i> |                 |                  |                             |                 |                  |                             |                 |                  |                             |
| United States .....                   | ....            | ....             | ....                        | 800             | 28.57            | 1.58                        | 3,400           | 38.20            | 6.72                        |
| Europe and Canada .....               | 2,000           | 100.00           | 9.62                        | 2,000           | 71.43            | 9.62                        | 5,500           | 61.80            | 26.46                       |
| Total .....                           | 2,000           | 100.00           | 2.88                        | 2,800           | 100.00           | 4.04                        | 8,900           | 100.00           | 12.83                       |

\*Plants using straight liquid sulfur dioxide have a total capacity of 92,260 bbl. per day; petroleum products such as kerosene.

In extracting oils with solvents the following types of processes are feasible:

1. Single solvent processes wherein the solvent consists of one chemical substance only.
2. Mixed solvent processes wherein the solvent consists of more than one chemical substance, and
3. Double solvent processes wherein the oil is dissolved in a solvent not miscible with the solvent used for extracting the impurities, this solution being extracted with a single or mixed solvent.

The following table shows the gradual increase in the solvent refining capacity of lubricating oil plants in the United States and abroad.<sup>27</sup>

These plants were distributed among the individual oil companies as shown in Table 25.

Refining Plants Producing Lubricating Oils

| January 1935                           |                     |                                   | January 1936       |                     |                                   | January 1937       |                     |                                   | January 1938<br>(Estimated) |                     |                                   |
|--|---------------------|-----------------------------------|--------------------|---------------------|-----------------------------------|--------------------|---------------------|-----------------------------------|-----------------------------|---------------------|-----------------------------------|
| Barrels Per<br>Day                     | Total<br>(Per Cent) | Present<br>Capacity<br>(Per Cent) | Barrels Per<br>Day | Total<br>(Per Cent) | Present<br>Capacity<br>(Per Cent) | Barrels Per<br>Day | Total<br>(Per Cent) | Present<br>Capacity<br>(Per Cent) | Barrels Per<br>Day          | Total<br>(Per Cent) | Present<br>Capacity<br>(Per Cent) |
| <i>United States</i>                   |                     |                                   |                    |                     |                                   |                    |                     |                                   |                             |                     |                                   |
| 10,342                                 | 55.18               | 68.71                             | 13,022             | 28.57               | 100.00                            | 13,022             | 26.81               | 100.00                            | 13,022                      | 26.81               | 100.00                            |
| 1,600                                  | 8.54                | 11.35                             | 11,100             | 24.36               | 78.72                             | 14,100             | 29.02               | 100.00                            | 14,100                      | 29.02               | 100.00                            |
| 4,500                                  | 24.01               | 73.17                             | 10,500             | 23.04               | 100.00                            | 10,500             | 21.62               | 100.00                            | 10,500                      | 21.62               | 100.00                            |
| 1,500                                  | 8.00                | 100.00                            | 6,150              | 13.50               | 100.00                            | 6,150              | 12.66               | 100.00                            | 6,150                       | 12.66               | 100.00                            |
| 800                                    | 4.27                | 100.00                            | 1,500              | 3.29                | 100.00                            | 1,500              | 3.09                | 100.00                            | 1,500                       | 3.09                | 100.00                            |
|  |                     |                                   | 2,500              | 5.49                | 100.00                            | 2,500              | 5.15                | 100.00                            | 2,500                       | 5.15                | 100.00                            |
|  |                     |                                   | 800                | 1.75                | 100.00                            | 800                | 1.65                | 100.00                            | 800                         | 1.65                | 100.00                            |
| 18,742                                 | 100.00              | 37.04                             | 45,572             | 100.00              | 94.07                             | 48,572             | 100.00              | 100.00                            | 48,572                      | 100.00              | 100.00                            |
| <i>and Canada</i>                      |                     |                                   |                    |                     |                                   |                    |                     |                                   |                             |                     |                                   |
| 5,500                                  | 100.00              | 94.83                             | 5,500              | 68.92               | 94.83                             | 5,800              | 43.77               | 100.00                            | 5,800                       | 27.90               | 100.00                            |
|  |                     |                                   | 450                | 5.64                | 39.13                             | 1,150              | 8.68                | 100.00                            | 1,150                       | 5.53                | 100.00                            |
| 5,500                                  | 100.00              | 26.46                             | 7,980              | 100.00              | 38.39                             | 13,250             | 100.00              | 63.74                             | 20,786                      | 100.00              | 100.00                            |
| <i>the World</i>                       |                     |                                   |                    |                     |                                   |                    |                     |                                   |                             |                     |                                   |
| 10,342                                 | 42.66               | 45.98                             | 15,052             | 28.11               | 66.92                             | 17,612             | 28.49               | 78.30                             | 22,492                      | 32.43               | 100.00                            |
| 1,600                                  | 6.60                | 8.66                              | 11,100             | 20.73               | 60.11                             | 15,810             | 25.57               | 85.62                             | 18,466                      | 26.63               | 100.00                            |
| 5,500                                  | 22.69               | 33.74                             | 16,000             | 29.88               | 98.16                             | 16,300             | 26.37               | 100.00                            | 16,300                      | 23.50               | 100.00                            |
| 4,500                                  | 18.56               | 73.17                             | 6,150              | 11.48               | 100.00                            | 6,150              | 9.95                | 100.00                            | 6,150                       | 8.87                | 100.00                            |
| 1,500                                  | 6.19                | 56.60                             | 1,950              | 3.64                | 73.58                             | 2,650              | 4.29                | 100.00                            | 2,650                       | 3.82                | 100.00                            |
| 800                                    | 3.30                | 100.00                            | 2,500              | 4.67                | 100.00                            | 2,500              | 4.04                | 100.00                            | 2,500                       | 3.60                | 100.00                            |
|  |                     |                                   | 800                | 1.49                | 100.00                            | 800                | 1.29                | 100.00                            | 800                         | 1.15                | 100.00                            |
| 24,242                                 | 100.00              | 34.95                             | 53,552             | 100.00              | 77.21                             | 61,822             | 100.00              | 89.13                             | 69,358                      | 100.00              | 100.00                            |
| <i>in the United States and Abroad</i> |                     |                                   |                    |                     |                                   |                    |                     |                                   |                             |                     |                                   |
| 18,742                                 | 77.31               | 37.04                             | 45,572             | 85.10               | 94.07                             | 48,572             | 78.57               | 100.00                            | 48,572                      | 70.03               | 100.00                            |
| 5,500                                  | 22.69               | 26.46                             | 7,980              | 14.90               | 38.39                             | 13,250             | 21.43               | 63.74                             | 20,786                      | 29.97               | 100.00                            |
| 24,242                                 | 100.00              | 34.95                             | 53,552             | 100.00              | 77.21                             | 61,822             | 100.00              | 89.13                             | 69,358                      | 100.00              | 100.00                            |

but they are not included in this summary, because they are used mostly for refining light

TABLE 25—Distribution of Solvent-Refining Plants

| Company                                     | Location                   | Charging Capacity Bbl./Day | Year of Construction |
|---|----------------------------|----------------------------|----------------------|
| <i>Duo-Sol Process</i>                      |                            |                            |                      |
| 1. Socony-Vacuum Oil Co., Inc.              | Paulsboro, N. J.           | 4,182                      | 1934                 |
| 2. Magnolia Petroleum Co.                   | Beaumont, Tex.             | 2,830                      | 1934                 |
| 3. Gulf Refining Co.                        | Philadelphia, Pa.          | 3,330                      | 1934                 |
| 4. Shell Petroleum Corp'n.                  | Wood River, Ill.           | 2,680                      | 1935                 |
| 5. Herbert Green & Co., Ltd.                | Hull, England              | 2,030                      | 1935                 |
| 6. Deutsche Vacuum Oel A.-G.                | Bremen, Germany            | 1,280                      | 1936                 |
| 7. Raffineries de la Vacuum Oil Co., S.A.F. | Port Jerome, France        | 1,280                      | 1936                 |
| 8. Socony-Vacuum Oil Co., Inc.              | Naples, Italy              | 1,280                      | constr.              |
| 9. Glavneft Oil Trust                       | Grozny, U. S. S. R.        | 3,600                      | constr.              |
| Total                                       |                            | 22,492                     |                      |
| <i>Furfural Process</i>                     |                            |                            |                      |
| 1. Indian Refining Co.                      | Lawrenceville, Ill.        | 1,600                      | 1933                 |
| 2. Gulf Refining Co.                        | Port Arthur, Tex.          | 5,000                      | 1935                 |
| 3. The Texas Co.                            | Port Arthur, Tex.          | 4,500                      | 1935                 |
| 4. Phatogen Raffineries de Petrole          | Roumania                   | 60                         | 1936                 |
| 5. Magnolia Petroleum Co.                   | Beaumont, Tex.             | 3,000                      | 1936                 |
| 6. Shell-Mex. B.P.                          | Shell Haven, England       | 1,650                      | 1937                 |
| 7. Gewerkschaft Deutsche Erdöl-Raffinerie   | Misburg, Germany           | 1,256                      | 1937                 |
| 8. Parent Petroleum Interests, Ltd.         | Dublin, Ireland            | 1,400                      | constr.              |
| Total                                       |                            | 18,466                     |                      |
| <i>Phenol Process</i>                       |                            |                            |                      |
| 1. Imperial Oil Co., Ltd.                   | Sarnia, Ont., Canada       | 2,000                      | 1929                 |
| 2. Standard Francaise de Petroles           | Port Jerome, France        | 3,500                      | 1933                 |
| 3. Standard Oil Co. of La.                  | Baton Rouge, La.           | 5,000                      | 1935                 |
| 4. Standard Oil Co. of N. J.                | Bayonne, N. J.             | 2,000                      | 1935                 |
| 5. Standard Oil Co. of Cal.                 | California                 | 3,500                      | 1935*                |
| 6. International Petroleum Co.              | Barranca Bermeja, Colombia | 300                        | 1936                 |
| Total                                       |                            | 16,300                     |                      |
| <i>Chlorex Process</i>                      |                            |                            |                      |
| 1. Standard Oil Co. of Ind.                 | Casper, Wyo.               | 600                        | 1932                 |
| 2. Mid-Continent Petroleum Corp'n.          | Tulsa, Okla.               | 200                        | 1932                 |
| 3. Standard Oil Co. of Ind.                 | Wood River, Ill.           | 1,000                      | 1933                 |
| 4. The Pennzoil Co.                         | Oil City, Pa.              | 1,000                      | 1934                 |
| 5. Socony-Vacuum Oil Co., Inc.              | Olean, N. Y.               | 1,700                      | 1934                 |
| 6. Bradford Penn Refining Corp'n.           | Clarendon, Pa.             | 450                        | 1935                 |
| 7. Freedom Oil Works Co.                    | Freedom, Pa.               | 1,200                      | 1935                 |
| Total                                       |                            | 6,150                      |                      |
| <i>Liquid Sulfur Dioxide-Benzol Process</i> |                            |                            |                      |
| 1. Union Oil Co. of Cal.                    | Oleum, Cal.                | 1,500                      | 1934**               |
| 2. Soc. Franc. des Huiles de Petr.          | Courchelettes, France      | 450                        | 1935                 |
| 3. "Aquila" S. A. Technico Industriale      | Trieste, Italy             | 700***                     | 1937                 |
| Total                                       |                            | 2,650                      |                      |
| <i>Nitrobenzene Process</i>                 |                            |                            |                      |
| 1. The Atlantic Refining Co.                | Philadelphia, Pa.          | 2,500                      | 1935                 |
| Total                                       |                            | 2,500                      |                      |
| <i>Nitrobenzene-Sulfuric Acid Process</i>   |                            |                            |                      |
| 1. Sinclair Refining Co.                    | Wellesville, N. Y.         | 800                        | 1934                 |
| Total                                       |                            | 800                        |                      |

\* Originally designed for aniline.

\*\* Built in 1926 for refining kerosene with liquid sulfur dioxide.

\*\*\* Plants employing liquid sulfur dioxide for refining kerosene, light lubricating oil distillates and naphtha have a total capacity of 92,260 bbl./day. The capacity of solvent refining plants at the present time for all types of petroleum products is, therefore, 161,618 bbl./day.

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## Chapter XI

### Variables Involved in Refining Oils with Selective Solvents

*(In collaboration with Th. A. Petry)*

Theoretical foundations of the selective solvent refining processes discussed in the previous chapter show that a great number of variables are encountered in practical applications of these processes which are discussed in detail in this chapter. These variables may be segregated in the following groups:

1. Nature of the solvent used,
2. Quantity of solvent employed,
3. Temperature of extraction,
4. Time of contacting the oil with the solvent,
5. Time of settling,
6. Method of contacting the oil with the solvent,
7. Nature of the oil extracted.

Many conflicting statements are frequently found in the literature concerning the relative effect of the above variables as most of them are interdependent and a considerable amount of systematic work is still required in order to elucidate the subject completely. The discussion below is an attempt to systematize the present knowledge on this subject as applied to practical solvents.

A very interesting discussion of the solvent refining processes is given by Hersh,<sup>1</sup> and by Poole.<sup>2, 3, 4</sup> Wilson and Keith<sup>5</sup> discuss economic aspects of solvent refining. Other articles of similar nature include those by Dickinson,<sup>6</sup> Consolati,<sup>7</sup> Wiggins and Hall,<sup>8, 9</sup> Wilson and Keith,<sup>10</sup> Fürst,<sup>11, 12, 13</sup> Ward and Forrest,<sup>14</sup> Garner and Van Dyck,<sup>15</sup> Kyropoulos,<sup>16</sup> etc. The superiority of motor oils prepared by the solvent refining methods as compared to those prepared by the conventional sulfuric acid methods is pointed out by Merrill, Moore, and Bray;<sup>17</sup> Auld;<sup>18, 19</sup> Ramser and Krekeler;<sup>20</sup> and others.

In defining the "impurities" removed by solvents it should always be remembered that they cannot be regarded as a fixed substance, because, as already mentioned, the oil is composed of an infinite variety of chemical compounds which show only a very gradual change in their properties from the so-called aromatic to the so-called paraffinic type. The desired properties of the finished oil therefore define the border line between these substances so that in certain instances the desirable components in products requiring only mild refining conditions may become undesirable when the

oil must be refined to a greater depth. Thus, by careful refining of a light Pennsylvania distillate to viscosity index specifications, the maximum yield of the 120 viscosity index oil of 78% was obtained. The remaining extract could be re-refined, however, with solvents under different optimum conditions of extraction yielding an additional 11% of an oil of a 95 viscosity index. Similarly by a more drastic extraction of the above extract 2% of an oil having the viscosity index of 110 was obtained.

### Nature of Solvent Used

In differentiating the relative efficiencies of various refining solvents in removing the undesirable constituents from petroleum oils, the solvents are frequently classified on the basis of their selectivity with respect to these constituents and the desirable oil fractions. The most selective solvent is considered to be the one which is capable of removing the minimum quantity of these constituents when effecting a given improvement in the lubricating oil stocks.

It should be noted, however, that solvents may differ from one another both with respect to their selectivity, *i.e.*, the value of the overall distribution coefficient for the low and high viscosity index constituents, and to their absolute solvent power towards these constituents, other conditions being constant. The value of the distribution coefficient controls the relative quantities of the impurities removed from the oil while the solvent power determines the magnitude of this removal.

Due to the absence of a sharp demarkation line between the desirable and undesirable constituents of the oil, the difference between the distribution coefficient and the solvent power of a solvent is usually obscured. However, in a general way increased solvent power is immediately associated with a change in the yield of the oil phase, while increase in selectivity is evidenced by a change in the relative properties of the two phases due to reasons already presented. The realization of the existence of these two variables is important, however, for properly portraying the mechanism of solvent extraction processes.

The difference between the selectivity and solvent power of solvents can be further illustrated by the following examples obtained in refining with various solvents a Coastal distillate of 65 Saybolt Universal seconds at 210° F., and 20 viscosity index, by single batch extractions.

TABLE 26—Difference Between Selectivity and Solvent Power

| Solvent<br>% by Volume | Temperature<br>of Extraction | Raffinate |                 |
|------------------------|------------------------------|-----------|-----------------|
|                        |                              | Yield     | Viscosity Index |
| 100% aniline           | 75° F.                       | 88%       | 35              |
| 50% nitrobenzene       | 35° F.                       | 78%       | 35              |
| 200% aniline           | 75° F.                       | 85%       | 39              |
| 45% nitrobenzene       | 35° F.                       | 85%       | 33              |
| 100% aniline           | 75° F.                       | 88%       | 35              |
| 100% nitrobenzene      | 35° F.                       | 66%       | 47              |

The above data permit us to draw the following conclusions with respect to the solvent properties of aniline at 75° F. and nitrobenzene at 35° F., when applied to the above Coastal distillate: nitrobenzene is shown to be less selective than aniline because the yield of the same quality of raffinate at 35 viscosity index is less when nitrobenzene is used, and because, in treating to equal yields of 85%, the viscosity index of the nitrobenzene raffinate is lower than that of the aniline raffinate. However, the solvent power of nitrobenzene is considerably greater than that of aniline because the yields of raffinates are the same when the oil is refined either with 200% of aniline or with 45% of nitrobenzene. The combined effect of selectivity and solvent power may be illustrated by the results obtained in applying equal percentages of the two solvents to the oil (100%). At the above temperatures the degree of improvement observed with nitrobenzene is greater than that with aniline but the yield is considerably smaller than that which can be expected if the oil were treated to the same viscosity index with aniline. Under the above conditions of extraction, however, the quantity of aniline required to raise the viscosity index of the oil to that obtained with 100% nitrobenzene is prohibitive being, probably, above 1000% which makes its application impractical. For these reasons in preparing an oil of a relatively low viscosity index, aniline at 75° F. would be preferred, while for a relatively high viscosity index oil nitrobenzene at 35° F. is more practical.

By choosing other extraction temperatures the difference between the two solvents may become more or less pronounced. The above temperatures were arbitrarily chosen. However, they are about 40° F. below the miscibility temperatures for these solvents and the Coastal distillate employed.

Another comparison between selectivity and solvent power characteristics of the different solvents is presented in the following table.<sup>21</sup>

TABLE 27—Single Batch Extraction with Chlorex,\* Nitrobenzene† and Acetone‡  
(200 volumes solvent used to 100 volumes oil, in all cases)

|                     | Original Oil | Chlorex Raffinate | Chlorex Extract | Nitrobenzene Raffinate | Nitrobenzene Extract | Acetone Raffinate | Acetone Extract |
|---------------------|--------------|-------------------|-----------------|------------------------|----------------------|-------------------|-----------------|
| Viscosity at        |              |                   |                 |                        |                      |                   |                 |
| 210° F.             | 49.          | 49.               | 55.             | 48.                    | 53.                  | 48.               | 52.             |
| 100° F.             | 272.         | 233.              | 582.            | 216.                   | 406.                 | 236.              | 390.            |
| Viscosity index     | 77.5         | 104.0             | 5.4             | 104.5                  | 54.1                 | 89.4              | 49.8            |
| V. G. C.            | 0.845        | 0.828             | 0.898           | 0.819                  | 0.817                | 0.833             | 0.891           |
| Gravity A.P.I.      | 25.8         | 28.5              | 18.0            | 29.8                   | 21.8                 | 27.7              | 19.8            |
| A.S.T.M. pour point | 0° F.        | 5° F.             | -10° F.         | 5° F.                  | -10° F.              | 0° F.             | -15° F.         |
| Yield, volume %     | 100.0        | 74.8              | 25.2            | 51.1                   | 48.9                 | 79.2              | 20.8            |

\* Miscible at 120° F.; extraction at 77° F.

† Miscible at 93° F.; extraction at 50° F.

‡ Miscible at 120° F.; extraction at 80° F.

Note: Liquid Sulfur Dioxide is an example of an extremely selective solvent of very low solvent power. Forty-three equal applications of Sulfur Dioxide (on an untreated Salt Creek stock) for a total of forty-six volumes of solvent to one

volume of oil, produced a raffinate of 61.0 V. I. and an extract of — 200 V. I. Hence the quality of the raffinate, even after this excessive extraction, is still unsatisfactory, although the V. I. difference, or "selectivity" is 261.0.

The above results again show the desirability of an optimum balance between selectivity and solvent power. By employing very large quantities of liquid sulfur dioxide a raffinate can be obtained which is similar in its properties to the raffinate from extracting the same oil with other solvents such as chlorex, nitrobenzene, or acetone. The use of such large quantities of solvent is prohibitive, however, commercially and, for this reason, by applying liquid sulfur dioxide to refining of lubricating oils its solvent power is increased artificially by blending it with benzol as discussed in the next chapter on mixed solvents.

Summarizing the above discussion it is evident that solvents possessing equal selectivities but different solvent power will yield raffinates and extracts of the same quality when the solvent to oil ratios are adjusted so as to give equal yields of the raffinate and extract phases. The larger the volume of the solvent required for this purpose, the less is the solvent power of the solvent, provided the method of applying the solvent to the oil is the same. Likewise, solvents possessing equal solvent power but different selectivities will yield equal quantities of raffinate and extract phases when they are applied to the oil in equal amounts, but the difference between the properties of the raffinate and extract phases will be less for a solvent possessing a lesser degree of selectivity.

### Quantity of Solvent

The quantity of solvent used has, obviously, a direct bearing on the yield and properties of the resulting raffinates. Thus in refining by single

TABLE 28—Effect of Quantity of Solvent Used in Refining

| Solvent<br>% by Volume      | % Yield | Gravity<br>A.P.I. | Raffinate<br>S. U. V. at<br>210° F. | Viscosity<br>Index | Carbon<br>Residue |
|-----------------------------|---------|-------------------|-------------------------------------|--------------------|-------------------|
| Original stock              | 100.0   | 21.4              | 130.0                               | 65.0               | 2.9               |
| <i>Furfural at 200° F.:</i> |         |                   |                                     |                    |                   |
| 300                         | 75.2    | 25.7              | 108.6                               | 84.7               | 1.1               |
| 600                         | 62.6    | 26.6              | 107.8                               | 88.6               | 0.9               |
| 900                         | 53.3    | 27.1              | 107.0                               | 91.0               | 0.8               |
| 1200                        | 47.1    | 27.3              | 106.4                               | 93.2               | 0.7               |
| <i>Chlorex at 80° F.:</i>   |         |                   |                                     |                    |                   |
| 300                         | 70.0    | 26.0              | 108.8                               | 85.4               | 1.0               |
| 600                         | 59.1    | 26.9              | 106.2                               | 89.5               | 0.8               |
| 900                         | 50.4    | 27.5              | 104.6                               | 93.6               | 0.7               |
| 1200                        | 44.8    | 27.6              | 104.2                               | 95.7               | 0.6               |
| <i>Phenol at 150° F.:</i>   |         |                   |                                     |                    |                   |
| 300                         | 66.3    | 25.9              | 108.2                               | 87.5               | 1.0               |
| 600                         | 50.0    | 27.8              | 107.0                               | 92.8               | 0.8               |
| 900                         | 40.8    | 28.0              | 104.2                               | 95.4               | 0.7               |
| 1200                        | 34.0    | 28.2              | 104.0                               | 97.5               | 0.6               |

batch extractions, a partially deasphalted Mid-Continent cylinder stock of 130 Saybolt Universal viscosity at 210° F., 2.9 carbon residue, and a 65 viscosity index, results given in Table 28 were obtained.

### Temperature of Extraction

The effect of temperature is likewise very pronounced. It affects both the selectivity characteristics and the solvent power of the solvents. The solvent power always increases with the increase in temperature until the oil and solvent become completely miscible. Selectivity, however, usually decreases gradually, or else remains relatively constant over a certain temperature range, and then decreases rapidly as the miscibility region is approached. This is illustrated by the following data, obtained in extracting a Coastal distillate with 100% of aniline-benzol mixtures containing 10% benzol, at various extraction temperatures.

TABLE 29—Effect of Temperature on Selectivity and Solvent Power

| Temperature of Extraction | Yield | Viscosity Index |
|---------------------------|-------|-----------------|
| 32° F.                    | 90%   | 33              |
| 75° F.                    | 85%   | 40              |
| 100° F.                   | 80%   | 36              |

The data show that while the yield decreases continually as the extraction temperature is raised, the viscosity index of the raffinate first shows an increase and then a decrease. This maximum indicates an optimum balance between selectivity and solvent power of the solvent as applied to the above stock.

The table below gives similar data obtained by extracting an undewaxed residual stock from Mid-Continent crude of 93 Saybolt Universal seconds at 210° F., with chloraniline employing the single batch method of extraction. The dewaxed charging stock had 105 Saybolt Universal seconds at 210° F., and a viscosity index of 74. The data below refer to the oil extracted in the undewaxed state, but afterwards dewaxed to approximately +10° F. pour test. The yields refer to the undewaxed oil.

TABLE 30—Effect of Temperature on Extraction with Chloraniline

| Solvent<br>by Volume | Temperature<br>of Extraction | Raffinate |                 |
|----------------------|------------------------------|-----------|-----------------|
|                      |                              | Yield     | Viscosity Index |
| 400%                 | 75° F.                       | 37%       | 97              |
| 240%                 | 100° F.                      | 23%       | 97              |
| 300%                 | 75° F.                       | 43%       | 95              |
| 150%                 | 100° F.                      | 43%       | 90              |
| 150%                 | 75° F.                       | 64%       | 89              |
| 150%                 | 100° F.                      | 43%       | 90              |
| 400%                 | 75° F.                       | 37%       | 97              |
| 400%                 | 100° F.                      | 9%        | 104             |
| 900%                 | 75° F.                       | 31%       | 100             |

These data likewise indicate that the selectivity of chloraniline is higher at lower temperatures, but that due to its low solvent power at these temperatures excessive quantities of solvent are needed in order to obtain the desired degree of refining.

Obviously nothing is gained by applying the solvent at temperatures at which the selectivity is poor as the quantity of good oil rejected in the extract is considerable while the degree of the improvement obtained may be less than that at lower temperatures. The use of higher temperatures can be justified, therefore, only if they are necessary for improving the solvent power of the solvent or the settling rates of the solvent-oil mixtures.

The above discussion also shows that solvents should be compared among themselves at temperatures at which they are capable of displaying their best solvent power-selectivity properties. These temperatures are different for different solvents and can be determined only from the experimental results obtained with given solvent-oil mixtures. The best solvent power-selectivity properties will vary depending upon the properties specified for the finished oil.

### **Time of Contact**

The time of contacting the oil with the solvent should be sufficient for obtaining equilibrium conditions. The time required for this purpose is evidently inversely proportional to the degree of agitation employed, or, if contacting is effected by passing counter-currently the solvent and the oil in thin films, by the relative thickness and viscosity of such films. These variables depend entirely on the nature of the equipment employed and should be determined experimentally. In general, however, only moderate agitation is usually sufficient for obtaining equilibrium conditions in a relatively short time.

### **Time of Settling**

The time of settling is likewise dependent on the nature of the oil and the solvent and on the degree of agitation employed. For these reasons it also can be determined only experimentally for each particular type of equipment and for conditions of extraction. In general, the time of settling is considerably longer for oils containing wax or asphaltic substances in suspensions as they tend to act as emulsifying agents. Some of the solvents appear to emulsify less readily than others. Increased temperatures usually improve settling rates due to lowered viscosities, provided the degree of dispersion of solvent and oil are the same.

If the separation between the raffinate and extract phases is not sufficiently rapid by gravity settling, centrifuging may be also resorted to.<sup>22</sup>

This is less desirable, however, as it increases the cost of the solvent refining equipment, unless the centrifuge cost is offset by elimination of settling drums and reduction of solvent and oil inventories in the extraction system.

### Method of Contacting

As already mentioned in Chapter X it is never possible to obtain the best separation of the oil into two fractions by single batch extractions with fresh solvents. Counter-current extraction methods are therefore always used in practice in order to insure maximum recovery of the desired product. The counter-current methods now in use include

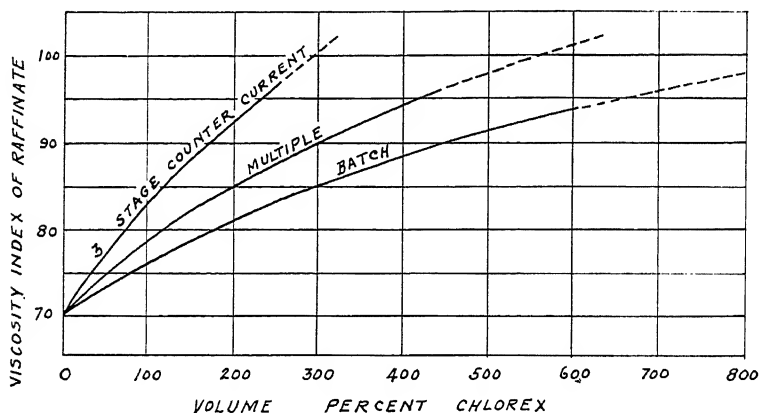


FIGURE 12.—Effect of Extraction Methods on the Amount of Chlorex Required to Produce an Oil of a Given Viscosity Index.

both multi-stage extractions, sometimes of batch but, usually, of continuous type, and counter-flow towers which have obvious advantages over the multi-stage extractors and should be used whenever possible.

Livingston and Dickinson,<sup>23</sup> Dickinson,<sup>6</sup> Rushton,<sup>24</sup> and Smith,<sup>25, 26</sup> describe an experimental solvent-extraction tower unit: various tower designs are covered by Manley and McCarty,<sup>27</sup> Poole,<sup>28</sup> Fenske and McCluer,<sup>29, 30, 31</sup> and others. Other counter-current extraction apparatus are likewise subject to many patents, such as Robinson,<sup>32, 33</sup> Houghton,<sup>34</sup> etc. Moor<sup>35</sup> describes a laboratory seven stage counter-current treating apparatus.

The use of towers is limited, however, to mixtures which contain no solid or semi-solid particles such as partially precipitated wax or asphalt, as these tend to interfere with the free flow of fluids through the narrow passages which are required in towers to insure an intimate contact between the two phases.

The advantages of counter-current extraction processes are further illustrated by the data plotted in Figure 12 showing the results of batch,

multiple and three stage counter-current extraction methods as applied to an SAE 50 grade of lubricating oil.<sup>21</sup> For this reason the discussion below is concerned mainly with the counter-current methods of applying solvents to the oils.

In considering the counter-current methods two definitions are possible for solvent to oil ratios: one definition based on the quantity of fresh solvent with which the oil is brought into contact, and another definition based on the total quantity of solvent employed in all stages irrespective of whether the solvent is fresh or partially spent. Thus, assuming that the oil is contacted with 200% fresh solvent in the last extraction stage and that the number of extraction stages is four, according to the first definition the oil is contacted with 200% of solvent and according to the second definition the oil is contacted with  $200\% \times 4 = 800\%$  solvent. In comparing the effectiveness of the counter-current methods it is therefore possible to base such comparisons either on the quantities of fresh solvent employed in extractions or on the quantities of total amount of solvent used by dividing this total amount into the number of extraction stages employed and by using the fresh solvent in these proportionate quantity. Although the second definition finds application in analyzing certain types of extraction problems, the first definition is used in all discussions herein, as it is the one widely accepted by the industry. Data plotted in Figure 13 show the difference in these definitions when applied to multi-stage extractions of a Mid-Continent stock of 130 Saybolt Universal seconds at 210° F., 65 viscosity index, and 2.9 carbon residue.

When the oil is contacted counter-currently with the solvent the sharpness of the separation between the desirable and undesirable constituents increases with increasing number of stages, but the introduction of each additional stage results in progressively smaller improvement in the quality of the raffinate. The number of extraction stages required to obtain a given degree of separation, as determined by yield-quality relationship, depends on the selectivity characteristics of the solvent, more selective solvents requiring a fewer number of extraction stages than the less selective ones. Figures 14, 15, and 16 show the results of extracting with three such diversified solvents as furfural, chlorex and phenol by single and three stage counter-current extraction methods, of a dewaxed and deasphalted Mid-Continent residuum of 130 Saybolt Universal seconds at 210° F., 65 viscosity index, and 2.9 carbon residue, the same which was employed in multi-stage extractions shown in Figure 12. The data show that in single stage extractions the solvents show considerable differences with respect to yields of a given quality product. These differences are very small, however, when comparisons are made employing the three stage extractions. If the number of extraction stages is further increased, even these differences tend to disappear and products of the same quality, as shown by their viscosity indexes, are obtained by



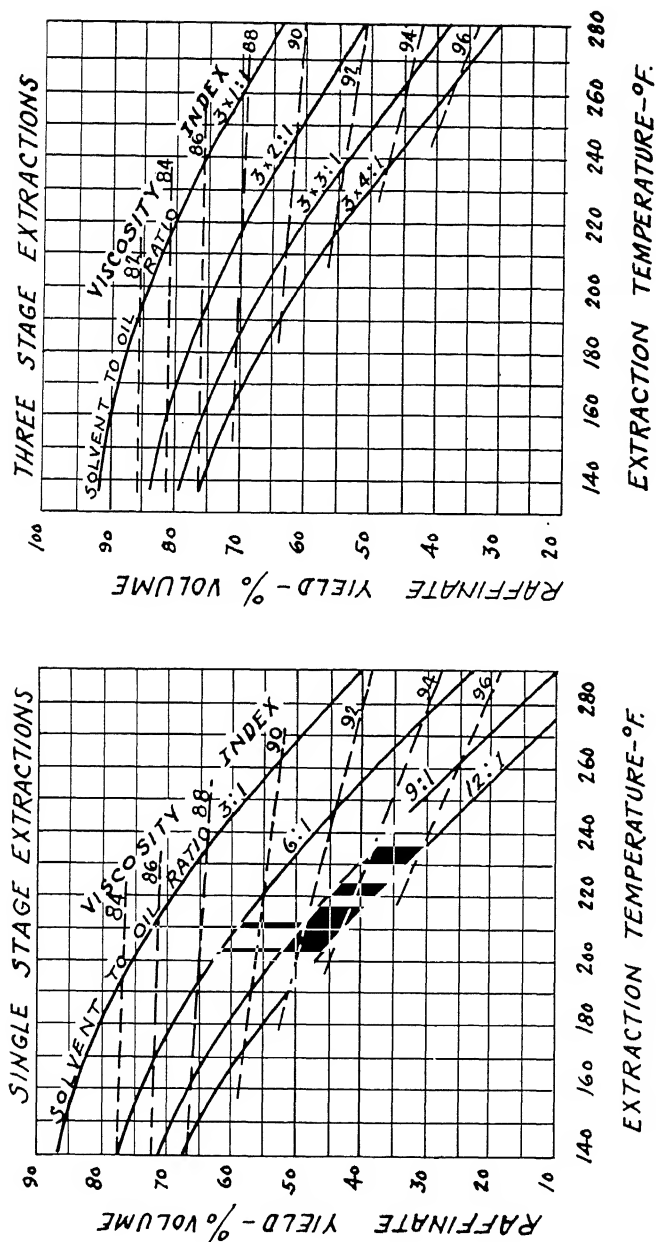


FIGURE 14.—Effect of Solvent to Oil Ratio on the Yield and Viscosity Index of the Furfural Treated Products (Dewaxed and Deasphalted Mid-Continent Residuum).

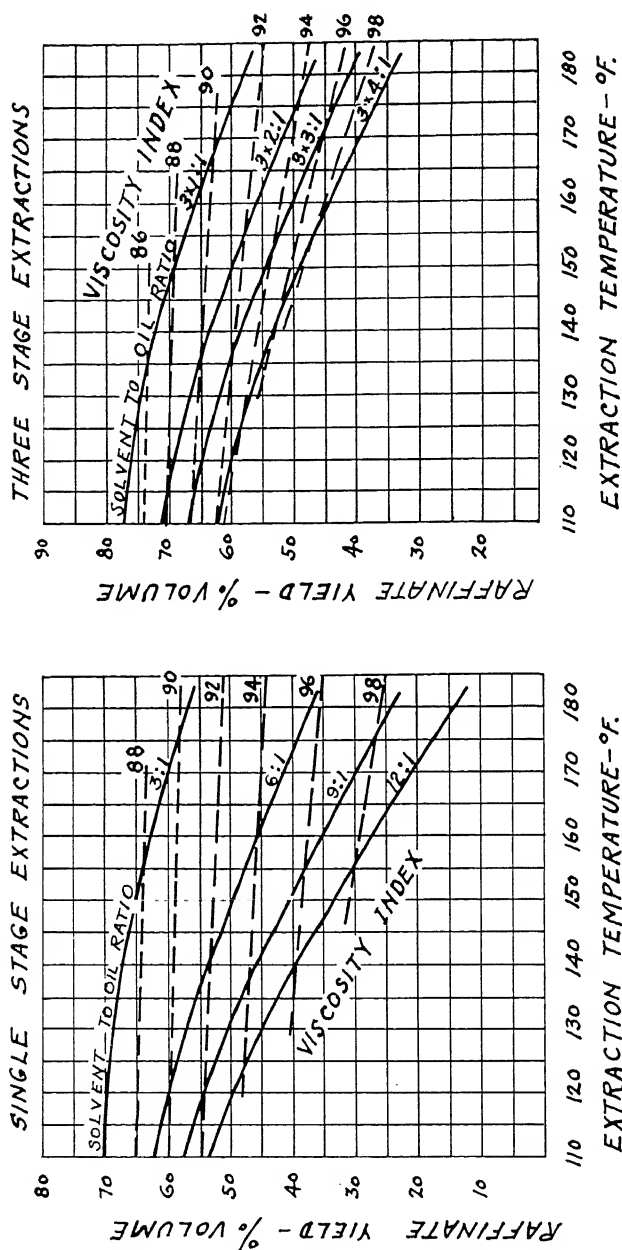


FIGURE 15.—Effect of Solvent to Oil Ratio on the Yield and Viscosity Index of the Phenol Treated Products (Dewaxed and Deasphalted Mid-Continent Residuum).

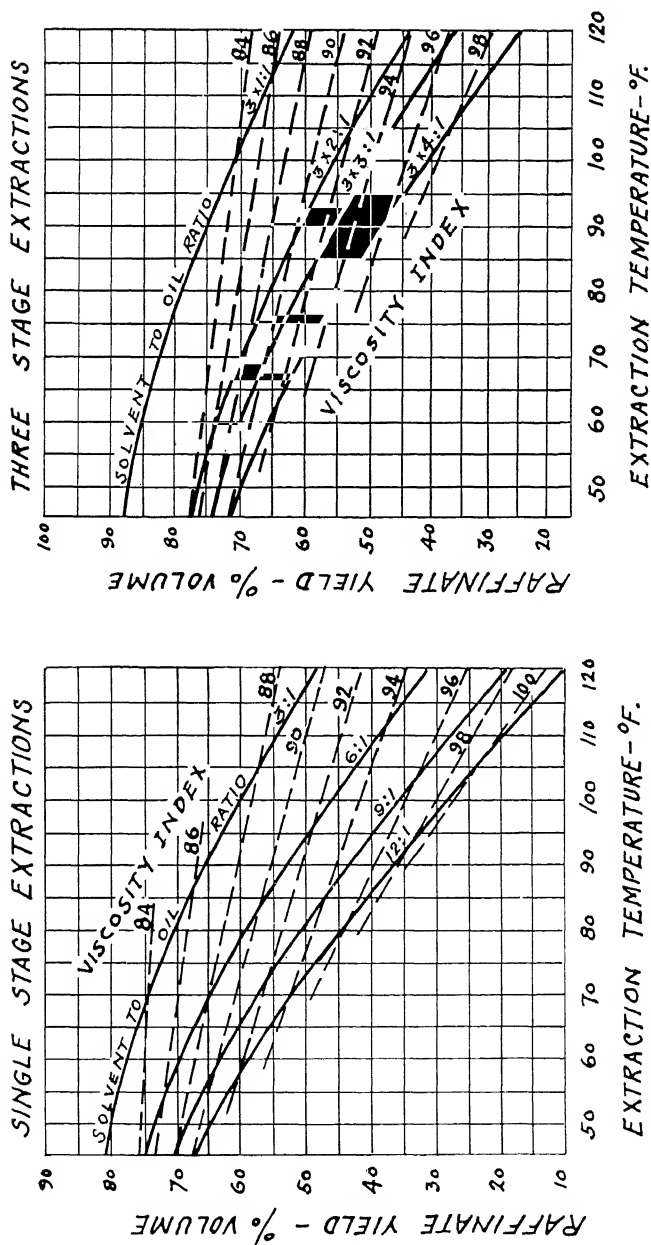


FIGURE 16.—Effect of Solvent to Oil Ratio on the Yield and Viscosity Index of the Chlorox Treated Products (Dewaxed and Deasphalted Mid-Continent Residuum).

extracting the oil with any of the three solvents and at practically the same refining yields provided the conditions of extraction are properly adjusted for the individual solvents. The cost of the solvent and the size of the extracting and solvent recovery equipment required for operation under these conditions would then become the deciding economic factors.

The above comparisons are made on the basis of the viscosity indexes of the raffinates. Similar results are observed also in treating oils to carbon residue or color specifications, although in exceptional instances some solvents may show better selectivity than others with respect to these types of oil constituents. This is, apparently, associated not so much with the preferential solubility characteristics of such solvents as with their ability to act as mild precipitating agents, as discussed in the chapter on deasphalting.

The above comparisons between the number of extraction stages employed or the nature of the solvent used are based primarily on the viscosity indexes of the resulting products which were taken as being representative of the oil quality. Although this is frequently permissible, it should be noted that an oil of the same viscosity index might be obtained by either single or multi-stage extraction methods, but in the first instance the separation between the desirable and undesirable constituents is less sharp than in multi-stage extractions. For these reasons, in referring to raffinates of equal quality on the basis of a single test, some confusion frequently results as other properties of the raffinates are considered to be the same also, which is not necessarily true. Single stage extractions will always give a somewhat different product than multi-stage extractions, and the uniformity of the product is obtained only after the number of extraction stages reaches a certain minimum beyond which further increase in the number of stages results only in a negligible improvement in the efficiency of separation.

The minimum quantity of solvent which can be used for extraction is defined by the solubility of the solvent in the oil, and the maximum quantity by the solubility of the oil in the solvent, as otherwise the separation into two phases is impossible. By raising the extraction temperature the mutual solubilities of solvent and oil increase until they become miscible in all proportions. In general, however, by increasing the temperature below the miscibility region the relative quantity of the oil dissolved in the extract phase is usually higher than that of the solvent in the raffinate phase, which for a relatively large temperature interval may be considered as being more or less constant. In counter-current extraction systems, miscibility conditions are first reached at the point where the partially spent extract is brought in contact with the fresh portion of oil, as under these conditions the relative proportion of the oil constituents highly soluble in the solvent reaches a maximum. Occasionally, also, when using very small quantities of solvents, the separa-

tion of the two phases is difficult, but this can be often remedied by recirculating the extract rejected from the system through the extraction stages where this difficulty is observed.

### Nature of Oil Extracted

Oils to be extracted with solvents vary considerably in their physical characteristics and in the relative contents of the desirable and undesirable constituents. Oils of Pennsylvania type contain more high viscosity index constituents than oils of Mid-Continent and particularly of Coastal type and, if products of equal viscosity index should be made, the Pennsylvania oils will yield the largest and the Coastal oils the smallest amounts of such products. In refining Mid-Continent stocks, the quantity of low viscosity index constituents which should be rejected for obtaining a product of viscosity index specifications similar to those of Pennsylvania oils is not commercially prohibitive, but in refining Coastal

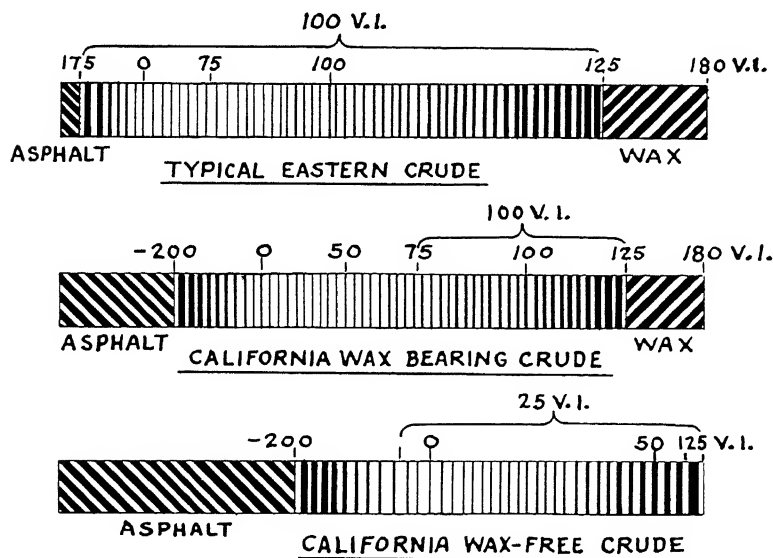


FIGURE 17.—Approximate Composition of Various Crude Residua.

stocks to the same specifications the yield of such quality oils may be reduced to an impractical minimum. For this reason, selection of stocks for solvent refining operations is important, as not all of them are able to give commercial yields of desired products. This is illustrated graphically in Figure 17, which compares approximate contents of various viscosity index fractions in some of the crudes.<sup>38</sup> Although different oil stocks may be regarded as all containing certain quantities of the

various viscosity index constituents, it does not necessarily follow that all of the constituents of a given viscosity index are identical irrespective of the type of crude in which they are present.

As already mentioned, the high viscosity index constituents are less soluble in solvents than the low viscosity index constituents. For this reason, in counter-current extractions, raffinate layers from which some of the low index constituents have been removed in the lower extraction stages, require conditions resulting in greater solubility of oil in solvent than the original oil in order to obtain a similar degree of improvement in their properties as compared with that observed in lower extraction stages. Likewise, oils containing large proportions of relatively high viscosity index constituents require, for improving their quality by a given increment, extraction conditions resulting in greater solubility of oil in solvent than oils containing smaller quantities of such constituents. Various selective solvents differ in exhibiting their most desirable solvent characteristics with respect to temperature, which explains why some of these solvents are best adapted for refining oils of one or of another type. Solvents which display such characteristics at low temperatures are well adapted for extracting oils of Pennsylvania type, while oils which display them at high temperatures are more suitable for oils of Mid-Continent and, particularly, of Coastal type. However, it is frequently advantageous to employ solvents requiring relatively high extraction temperatures as, for instance, in extracting wax bearing stocks such extractions may be performed at temperatures at which the wax is in the liquid state and does not interfere with extractions by introducing emulsification difficulties.

For the same reason, it is frequently desirable to subject an oil to a more drastic refining with solvents at the higher refining stages than at the lower ones, and improve the efficiency of extraction without increasing the number of extraction stages. This can be accomplished either by changing the nature or the composition of the solvent during extraction, or by maintaining a temperature gradient between the different extraction stages.

Kwal,<sup>37</sup> and Fussteig show the feasibility of extracting lubricating oils first with phenol and then with meta-nitrobenzyl alcohol; N. V. de Bataafsche Petroleum Maatschappij,<sup>38</sup> indicates the possibility of improving the properties of raffinates from liquid sulfur dioxide extractions by subsequent extractions with lower aliphatic acids; van Dijk<sup>39</sup> reextracts the liquid sulfur dioxide raffinates with a solvent comprising an organic compound, other than a nitrated monocyclic aromatic hydrocarbon, which contains a nitro group, such as nitro-methane, an organic compound other than a thiocyanate which contains a —CN group, such as propionitrile or benzonitrile, or with methyl thiocyanate; etc.

Edeleanu Ges. m.b.H.<sup>40</sup> maintains a higher temperature where the solvent enters the system and a lower temperature where the solvent leaves the system; Texaco Development Corporation<sup>41</sup> extracts oils selectively with furfural which may be diluted with benzol, toluol or light petroleum hydrocarbons by maintaining a graduated range of temperatures throughout the extraction stages; etc. See also Merrill and Subkow;<sup>42</sup> and Merrill.<sup>43</sup>

Under these conditions some of the oil is continually refluxed within the extraction system thus improving efficiency of extraction. The latter method is advantageous for plant use if the number of extraction stages employed is insufficient for obtaining a very sharp separation between the desirable and undesirable constituents. The same results can be obtained, however, without introducing such additional refluxing provided the number of extraction stages is increased to the required optimum.

Effect of reflux on the quality of products obtained from continuous counter-current extractions of oils with solvents with particular reference to tower extractions, are given by Hersh.<sup>3</sup>

In establishing the temperature gradient at a constant extract exit temperature care should be exercised not to exceed certain limits. The temperature at the rejection point of the system is of primary importance in determining the quality and yield of the raffinate phase. If the temperature at the raffinate end is excessively high, deterioration of the product may occur due to a possible close approach to the miscibility temperature where the raffinate leaves the system.

### Separation of Solvents from the Oil

Solvents are usually separated from the oil by distillation as seen in Chapter X under the discussion of the requirements which must be met by an ideal solvent. It is also feasible, however, to separate the solvent from the oil by extracting the raffinate or the extract phase with a second solvent which is more miscible with the selective solvent than with the hydrocarbon. However, only some very unusual properties of the primary solvents can warrant such a procedure on economic grounds since additional steps are introduced into the operations. Such secondary solvents may include ketones,<sup>44</sup> liquid sulfur dioxide,<sup>45</sup> alcohols,<sup>46</sup> or substances of the similar type. This method is essentially the same as that described in connection with the separation of water from solvents by preferential solubilities in a subsidiary solvent.

In commercial recovery units a sharp separation between the solvent and the oil is of considerable importance. If some of the oil is left in the solvent the solubility characteristics of the solvent are altered while if the solvent is left in the oil it increases the cost of refining as the solvent is thus lost from the system. The presence of solvent in the oil may likewise reflect upon the oil quality if this solvent is not subsequently removed by finishing operations. It is, therefore, important to control the quantity of solvent left both in the raffinate and in the extract after the separation is accomplished.

If the quantity of solvent left in the oils is considerable, its measurement can usually be accomplished by careful laboratory fractionation of the mixture, by estimating the quantity of solvent in the oil from

gravity measurements, by chemical analysis, etc.\* When the quantity is small, however, the above methods may not be capable of giving satisfactory results and use is usually made of the lowering of the flash point of the oil by the presence of such traces of solvents. For improving the accuracy of this method, flash points are determined in close-cup flash point equipment.† This method is of considerable assistance when the quantity of solvent in the oil is not over 0.5%. In practice, the curves showing the relation between the flash point of oils and the quantity of solvent present are determined for individual solvent and oil mixtures prepared synthetically. Within certain limits it might be assumed that this flash point lowering is independent of the nature of the oil being related only to the flash point, but for careful determinations of the solvent content this cannot be considered as strictly correct.

Careful laboratory measurements showed, for instance, that adding 0.1% of furfural to a Mid-Continent cylinder stock of 480° F. flash point, and to a blend of Mid-Continent and Coastal stocks of 390° F., reduced both flash points to 340° F. Addition of 0.2% of chlorex to the same stocks reduced their flash points to 340° F. Further equal additions of these two solvents resulted in lowering of the flash point of the 480° F. flash point stock, to a value below that of the 390° F. flash point stock. Notwithstanding these discrepancies, the method is of considerable importance in commercial practice being of sufficient accuracy for most practical purposes.

The above discussion applies to all of the selective solvent refining processes. These are described in more detail in the subsequent chapters which are concerned mainly with practical applications of such solvents to refinery needs.

\* Kurtz, Headington and Zieber,<sup>47</sup> describe the use of such methods as applied to nitrobenzene.

† Kurtz, Headington, and Zieber,<sup>47</sup> constructed a chart for estimating the quantity of nitrobenzene present in an oil from the lowering of the closed-cup flash point of such mixtures.

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## Chapter XII

### Single Solvents

Recent investigations have shown that a very large number of chemical compounds are capable of exhibiting a preferential solvent action towards the various constituents of petroleum. Of these compounds, liquid sulfur dioxide, chlorex, furfural, nitrobenzene and phenol have achieved commercial importance in single solvent processes, while aniline, in spite of its poisonous nature, may also become of future interest.

Besides the above solvents, a series of others have been covered by patents as being capable of displaying the required selective solvent properties. These solvents include benzonitrile,<sup>1</sup> furfuraldoxime,<sup>2</sup> benzaldehyde,<sup>3</sup> aliphatic aldehydes, particularly propionaldehyde,<sup>4</sup> lower aliphatic acids, such as acetic, propionic, butyric or *iso*-butyric,<sup>5</sup> *iso*-propyl alcohol,<sup>6</sup> furfuryl alcohol,<sup>7</sup> tetrahydrofurfuryl alcohol,<sup>8</sup> nitro alcohols such as nitrobenzyl alcohol,<sup>9</sup> ethylene glycol ethers and their acyl derivatives,<sup>10</sup> aromatic acetates, such as phenyl acetate,<sup>11</sup> or benzyl acetate,<sup>12</sup> methyl acetate,<sup>13</sup> esters of furoic acid, such as *iso*-propyl or butyl furoates,<sup>14</sup> methyl, ethyl or propyl amino benzoates,<sup>15</sup> aliphatic keto-esters such as ethylacetoacetate,<sup>16</sup> lower alkyl hydrogen sulfates,<sup>17</sup> diketones, such as acetyl acetone,<sup>18</sup> chlorinated substances, such as chlorohydrins,<sup>19</sup> chloroacetates,<sup>20</sup> etc., quinoline,<sup>21</sup> amines,<sup>22</sup> nitriles or organic thiocyanates,<sup>23</sup> acetonitrile,<sup>24</sup> aromatic cyanides, such as phenyl cyanide,<sup>25</sup> nitro or nitrile derivatives of aliphatic hydrocarbons, such as nitromethane,<sup>26</sup> tetrahydrofuran,<sup>27</sup> benzoyl-, tolyl-, or xyloylfuran,<sup>28</sup> aliphatic acyl derivatives of furan, such as acetylfuran,<sup>29</sup> chloraniline,<sup>30</sup> acetophenone,<sup>31</sup> carvacrol,<sup>32</sup> liquid trimethylene,<sup>33</sup> liquid ammonia,<sup>34</sup> liquid carbon dioxide,<sup>35</sup> liquid hydrogen sulfide,<sup>36</sup> dibutyl sulfone,<sup>37</sup> and many others.\* This list is increasing continually, as the number of substances which may be employed as selective solvents for petroleum oils, is by no means small. It appears possible that at least some of the substances enumerated above may, with time, become commercially important, particularly, if they can be obtained at a low cost.

#### Liquid Sulfur Dioxide Process

The success of the Edeleanu process in refining kerosenes resulted in a series of attempts to apply this solvent to the refining of lubricating oil

\* Some of the patents, such as those of Standard Oil Co. of Indiana,<sup>38, 39</sup> Edeleanu Ges. m.b.H.,<sup>40, 41</sup> or N. V. de Bataafsche Petroleum Maatschappij,<sup>42</sup> cover many hundreds of compounds which, according to their claims, can be used as selective solvents either alone or in mixtures with other solvents.

distillates. Brandt<sup>43</sup> and Kain<sup>44</sup> \* investigated the possibility of manufacturing motor, transformer and turbine oils by extraction with liquid sulfur dioxide. They found that the extracted oils have a flatter viscosity-temperature curve and produce less sludge and acidity in use; transformer oils become more resistant to oxidation; turbine oils emulsify less readily, etc. It has been also claimed that under certain conditions lubricating or other oils containing paraffin wax can be treated with liquid sulfur dioxide and the separated upper layer of wax can be filtered at the same low temperature to remove the crystallized paraffin.

N. V. de Bataafsche Petroleum Maatschappij,<sup>47</sup> and Frank,<sup>48</sup> describe results of refining transformer and turbine oils; Egloff<sup>49</sup> describes the preparation of lubricating oils from cracked residuum by sulfur dioxide extractions.

The resinous and asphaltic substances are also removed,<sup>50</sup> as well as the nitrogen bases.<sup>51</sup> Paraffin wax can be purified by extraction with liquid sulfur dioxide at temperatures above its melting point,<sup>52†</sup> or by flowing the liquid sulfur dioxide over the surface of solid paraffin, the oily matter adhering to the paraffin being dissolved and removed without the necessity of filtering.<sup>54</sup> Apparently, however, liquid sulfur dioxide has not been applied commercially to the refining of this product.

Sulfur dioxide ( $\text{SO}_2$ ) has the properties listed below.

TABLE 31—Properties of Sulfur Dioxide

|                                |                        |
|--------------------------------|------------------------|
| Molecular weight               | 64.12                  |
| Boiling point                  | 14° F.                 |
| Freezing point                 | − 105° F.              |
| Specific gravity at 68/68° F.  | 1.45                   |
| Specific heat                  | 0.32 B. t. u./lb./° F. |
| Heat of vaporization           | 167 B. t. u./lb.       |
| Vapor pressure at − 54° F.     | 100 mm.Hg.             |
| Vapor pressure at 100° F.      | 4370 mm.Hg.            |
| Solubility in water at 32° F.  | 19%                    |
| Solubility in water at 104° F. | 5%                     |
| Critical temperature           | 311° F.                |
| Critical pressure              | 79 atm.                |

Due to its low boiling point, pressure equipment is required in commercial plant installations.

Many patents have been issued at various times covering the specific application of liquid sulfur dioxide to the refining of lubricating oils,<sup>55</sup> but the degree of improvement in the properties of motor oils which can be obtained by this reagent is, within the commercial limits, not sufficient to warrant its use even when the extraction temperatures are raised to the

\* See also the interesting reviews by Edeleanu,<sup>53</sup> and Foster,<sup>46</sup> and succeeding articles giving an extensive discussion and a review of literature on the Edeleanu process.

† N. V. de Bataafsche Petroleum Maatschappij,<sup>53</sup> describes a similar method but employs low extraction temperatures.

maximum practical limit.\* A modified liquid sulfur dioxide process which involves the use of benzol in combination with the liquid sulfur dioxide was, therefore, developed and is described in Chapter XIII on mixed solvents.

The application of the Edeleanu process as well as of other solvent refining processes for the production of special oils, such as transformer and turbine oils, has been tried with more success and is now being used commercially.† The controversy exists, however, whether such oils are in reality superior to oils produced by the conventional sulfuric acid treating methods. This controversy is due primarily to the existence of a variety of oxidation tests which are employed for evaluating the quality of such oils in service, while the results obtained under actual service conditions lack convincing comparisons. Apparently, the solvent refined oils differ in their oxidation stabilities as measured by such laboratory tests from the sulfuric acid refined oils, but it seems premature to draw at the present time definite conclusions whether this is reflected in their higher or lower stability in service.

### Chlorex Process

This process was developed by the Standard Oil Co. of Indiana,<sup>50</sup> and is particularly adapted to the refining of Pennsylvania type of oils.

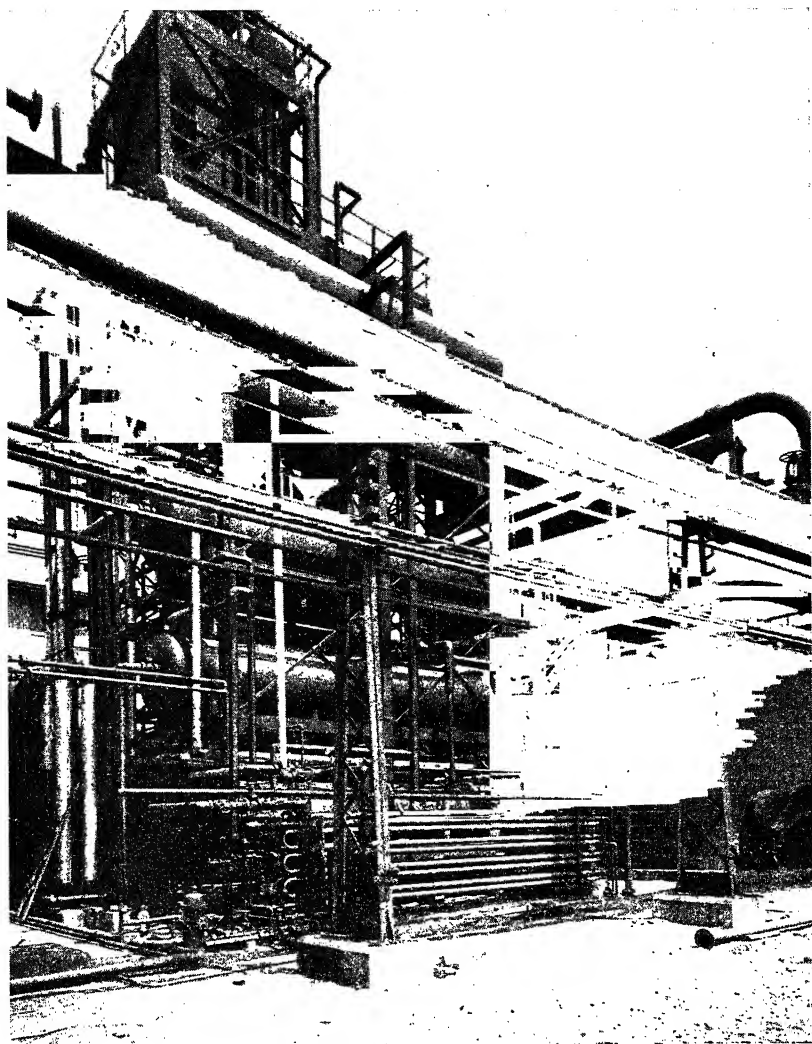
By 1936 seven commercial plants were using chlorex as a selective solvent. Four of these plants were designed for processing Pennsylvania stocks and are used by the Pennzoil Co., Freedom Oil Works Co., The Bradford Pennsylvania Refining Corp., and Socony-Vacuum Oil Co., Inc.

TABLE 32—Physical Properties of Chlorex

|                                    |  |
|------------------------------------|--|
| Molecular weight                   | 142.98                                 |
| Boiling point (760 mm.Hg.)         | 352.4° F. (178° C.)                    |
| Freezing point                     | — 61° F. (— 51.7° C.)                  |
| Viscosity:                         |  |
| Centipoises at 25.5° C.            | 2.0653                                 |
| Saybolt Universal 77° F. (25° C.)  | 32                                     |
| Saybolt Universal 32° F. (0° C.)   | 39                                     |
| Vapor pressure, mm.Hg.             | 2 at 100° F. (37.8° C.)                |
| Vapor pressure, mm.Hg.             | 100 at 242° F. (116.7° C.)             |
| Latent heat of vaporization        | 115.4 B. t. u./lb. or<br>64.1 cal./gm. |
| Specific heat at 85° F. (29.4° C.) | 0.369                                  |
| Flash point (closed cup)           | 168° F.                                |
| Solubility in water:               |  |
| 68° F. (20° C.)                    | 1.01%                                  |
| 194° F. (90° C.)                   | 1.71%                                  |
| Specific gravity                   | 1.222 at 68° F. (20° C.)               |

\* Extractions of lubricating oils at temperatures above 30° C. (86° F.), are specified by Rosenberg.<sup>50</sup>

† The Avon Refinery of the Associated Oil Co. has been described,<sup>51</sup> where these oils are manufactured by the liquid sulfur dioxide process. Velikovskii, Poznyak, and Semenidov,<sup>52</sup> discuss the possibilities of employing the process for manufacturing transformer oils.



*Courtesy: Carbide and Carbon Chemicals Corporation*

PLATE V.—Chlorex Solvent Refining Unit.

The solvent is, therefore, of the type which is mostly suitable to the refining of paraffinic type of oils due to the relatively high solvent power displayed at fairly low temperature extractions.

Chlorex is an abbreviated name for  $\beta'$   $\beta'$ -dichloroethyl ether ( $\text{CH}_2\text{Cl}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$ ) and has the physical properties given in Table 32.

Acidity of commercial chlorex is approximately 5.5 mg. of HCl per 100 cc. of chlorex. After hydrochloric acid is removed the recovered chlorex is claimed to be more stable than the fresh product. Traces of hydrochloric acid formed on distilling chlorex should be neutralized in order to prevent corrosion of the equipment. The solubility of water in chlorex is about 3% at room temperature.

The relatively high solvent power of chlorex requires somewhat low extraction temperatures which may require dewaxing the oil before solvent refining and make the solvent particularly useful in refining Pennsylvania or similar types of oils.

One commercial installation extracts waxy Mid-Continent type distillates below the wax melting point as regular practice. This can only be done, of course, by stage counter-current methods, not by tower counter flow, as wax tends to plug column packing materials.

Extractions are usually carried out between 30° F. and 80° F. with Mid-Continent stocks, and may be raised to 100° F. or 120° F. for oils such as Pennsylvania cylinder stocks. Under these conditions it is also claimed that the solvent may be applied to oils of a pour point as high as 120° F. without emulsification difficulties provided the settling time is sufficient.

The process is applied to Pennsylvania oils for improving the yields from clay percolation filters, or for raising their viscosity index, or for reducing carbon residue values or for some combination of these three objectives. On Mid-Continent stocks the primary object is that of raising the viscosity index to that of Pennsylvania oils. The yields in solvent refining evidently vary with the degree of improvement desired. They are considerably higher with Pennsylvania type of oils than with Mid-Continent stocks due to the differences in their contents of asphaltic matter and low viscosity index constituents.

In applying the process to Pennsylvania type of oils usually a four-stage counter-current extraction system of the simplest type is sufficient to insure satisfactory performance. Additional stages up to a total of seven may, however, be beneficial in raising the yield of the refined oil, where the price differential between oil and extract as fuel is large. Counter-current extraction towers are now also being developed. In counter-current multi-stage extractions the floor space can be saved by installing the horizontal settling tanks one above the other. The raffinate phase is then allowed to gravitate downwards while the extract phase is pumped upwards in the opposite direction.

Chlorex is recovered at 300-325° F. under a vacuum of 26-28 inches

Hg. with the use of smaller or larger quantities of steam. It is possible to remove chlorex from the condensed steam by extracting such solutions with oils or by flash distillation. Low distillation temperatures are desirable as some decomposition takes place at high temperatures which may result in corrosion of the equipment.

As in other processes, the solvent losses are now usually kept below 0.1%.

In refinery practice no attempts usually are made to remove the water dissolved in the chlorex.

### Furfural Process

The process has been developed by the Texas Oil Co. and the Royal Dutch Shell Co.,<sup>60</sup> and is used primarily in refining Mid-Continent stocks, although it might also be used conveniently with Coastal stocks at somewhat lower extraction temperatures, as well as with Pennsylvania stocks but at higher temperatures.

Due to its high miscibility temperature furfural is well suited for extraction at ordinary temperatures of light oils, which with other solvents may be miscible at these temperatures. Gross<sup>61</sup> thus applies furfural for refining of straight-run naphthas and a variety of other products.

Furfural or furfuraldehyde ( $C_4H_3O.CHO$ ) has the properties given below.

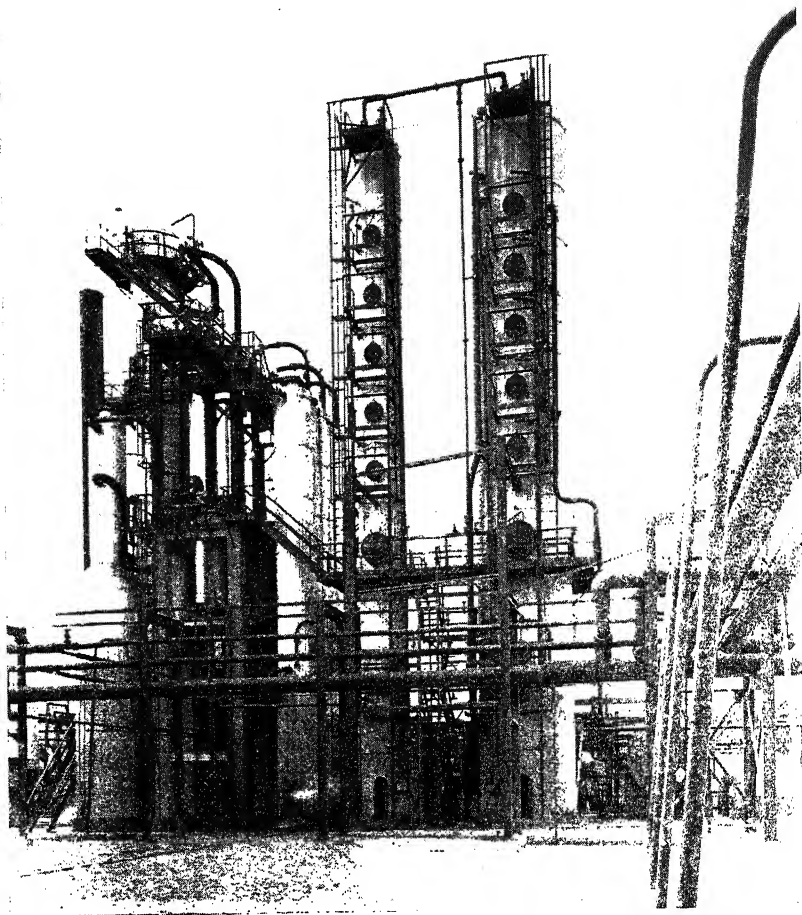
TABLE 33—Properties of Furfural

| Structural formula               | $  \begin{array}{c}  \text{CHO} \\  \text{CH} = \text{C} < \\    \\  \text{CH} = \text{CH} \diagup \text{O}  \end{array}  $ |
|----------------------------------|---|
| Molecular weight                 | 96.03   |
| Boiling point                    | 323° F.   |
| Freezing point                   | — 34° F.  |
| Specific gravity                 | 1.1622 at 20° C. (68° F.)   |
| Vapor pressure at 100° F.        | 7 mm.Hg.  |
| Vapor pressure at 216° F.        | 100 mm.Hg.  |
| Latent heat of vaporization      | 193.5 B. t. u./lb.  |
| Specific heat (68-212° F. range) | 0.416   |
| Flash point (closed cup)         | 138° F.   |
| Kinematic viscosity at 100° F.   | 0.907 centistokes   |
| Critical temperature             | 746° F.   |
| Critical pressure                | 798 lbs./sq. in. abs.   |
| Solubility in water at 100° F.   | 9.0%  |

Treating temperatures usually vary between 100° F. and 250° F. but for Mid-Continent oils they are somewhere around 200° F. Furfural is recovered from the oil at temperatures of about 450° F. although it is claimed that even higher temperatures can be used up to 550° F. without seriously decomposing the solvent.

The extract oil is frequently polymerized or condensed to give specific gravities and viscosities higher than those obtained by other solvents. The solvent does not appear to be a part of the polymerized molecule.

A rather interesting modification of the usual method of recovering oil from the furfural-oil solutions has been proposed by Manley.<sup>62</sup> The oil-



*Courtesy: Texaco Development Corporation*

PLATE VI.—Furfural Solvent Refining Unit.

furfural solutions are heated in admixture with water to about 275° F. at which temperature furfural becomes miscible with water, the oil being thereby displaced from the solution. The water-furfural mixture is then separated from the oil and chilled to about 80° F. at which temperature the water separates from furfural which is then used for further extractions.

Furfural is applied to the oil either in a multi-stage counter-flow manner or in counter-flow towers. Towers are packed with about 20 feet of Raschig rings with redistribution means at about each 4 feet of packed tower space. Charge rates should average about 35 gallons of charge oil per hour per square foot of overall tower cross-sectional area, although rates as high as 70 gallons per sq. foot per hour are claimed possible without incurring excessive entrainment. In counter-current batch extractions eight stages are usually employed.

The possibility of applying furfural in counter-flow towers makes this solvent quite attractive commercially. While the same principle can be applied to other solvents, the relatively high extraction temperatures in furfural refining permit the operation of the plants at temperatures considerably above those at which wax begins to separate out. For this reason no difficulty is experienced in settling out of the wax during extractions which with many other solvents may interfere with the efficient operation of towers. The general description of the principles involved in such extractions has already been described. In furfural treating towers, the temperature gradient which has been found to be commercially most efficient is usually maintained at 20-50° F. so as to permit sufficient internal reflux without undue lengthening of the column.

### Phenol Process

This process has been investigated for a number of years by various oil companies,\* but has been most extensively developed by the Standard Oil Co. (N.J.), through its subsidiary the Imperial Oil Co. of Canada, which employs anhydrous phenol instead of phenol containing a few per cent of water, as specified in most of the earlier patents.<sup>67</sup>

Phenol has the properties given below.

TABLE 34—Properties of Phenol

|                                 |                        |
|---------------------------------|------------------------|
| Molecular weight ( $C_6H_5OH$ ) | 94.05                  |
| Boiling point                   | 361° F. (183° C.)      |
| Melting point                   | 105.6° F. (44.9° C.)   |
| Vapor pressure at 251° F.       | 100 mm.Hg.             |
| Specific gravity at 68/68° F.   | 1.072                  |
| Specific heat                   | 0.56 B. t. u./lb./° F. |
| Heat of vaporization            | 206 B. t. u./lb.       |
| Flash point (closed cup)        | 174° F.                |
| Solubility in water at 77° F.   | 9%                     |
| Solubility in water at 151° F.  | infinite               |

\* Chem. Fabrik Lindenhof C. Weyl and Co.;<sup>68</sup> Kuczynski;<sup>61</sup> Frazer<sup>65</sup> uses phenol with 5-15% water; etc. Schick<sup>60</sup> uses phenol with many diluents.

The melting point of phenol is easily lowered by addition of water or a variety of other chemical substances.

The oil is contacted with phenol usually at 110-200° F., depending on the characteristics of the stock, although some oils may require temperatures as high as 250° F. As these temperatures are relatively high, it is usually possible to treat oils without removing the wax and to employ the counter-current treating towers similar to those developed for furfural. In treating towers, reflux is obtained by injecting water at the oil feed point, which improves the efficiency of extraction similarly to the improvement obtained by introducing the temperature gradient. The separation of water from phenol, which forms a constant boiling mixture containing 9% water, is accomplished by passing the vapors in counter-current flow to an untreated oil leaving as a residual vapor substantially pure water.

### Nitrobenzene Process

The nitrobenzene process was developed by the Atlantic Refining Company,<sup>68</sup> which is operating it now on a commercial scale.

Nitrobenzene ( $C_6H_5NO_2$ ) has the properties given below.

TABLE 35—Properties of Nitrobenzene

|  |                        |
|--|------------------------|
| Molecular weight                       | 123.5                  |
| Boiling point                          | 411.5° F. (211° C.)    |
| Melting point                          | 42.5° F. (5.8° C.)     |
| Vapor pressure at 100° F.              | 0.9 mm.Hg.             |
| Vapor pressure at 286° F.              | 100 mm.Hg.             |
| Specific gravity at 68/68° F.          | 1.207                  |
| Specific heat                          | 0.34 B. t. u./lb./° F. |
| Latent heat of vaporization            | 142 B. t. u./lb.       |
| Flash point (closed cup)               | 208° F.                |
| Its solubility in water is very slight |                        |

In its solvent power, nitrobenzene surpasses most of the other solvents and it is, therefore, particularly suitable to the refining of Pennsylvania type of oils, although other stocks also can be successfully treated with it. This is due particularly to the fact that the presence of wax in the oil at low temperatures when the wax separates out does not interfere with the separation into two phases to the same extent as with most of other solvents. Due to its high solvent power the extraction temperatures are relatively low and the quantity of solvent used is also small, usually in the range of 50-200%. Due to the low treating temperatures, slight refrigeration is frequently required. Nitrobenzene is usually recovered from the oil at temperatures about 350° F. by applying vacuum and steam. The high boiling point of the solvent makes, however, its separation from the lower boiling petroleum lubricating oil fractions more difficult than that of other solvents.

The nitrobenzene plant employs the so-called "cascade" system of contacting. The settling chambers are elevated above the ground and

the separated layers flow from them to the mixing pumps which transfer the mixtures to the next settling chambers. A five stage treating system is adopted at the plant.

The nitrobenzene plant operates on oils which are not necessarily deasphalted before solvent refining. As has been already mentioned, however, this is compensated by the use of additional quantities of clay or sulfuric acid and clay \* for further improvement of the color and carbon residue of the stocks.

A modification of the nitrobenzene process was developed by the Sinclair Refining Co. for refining lubricating oils, particularly of Pennsylvania type, by a simultaneous application of nitrobenzene and sulfuric acid.<sup>70</sup> Apparently, however, this modification of the process did not meet with a commercial success.

### Aniline Process

The aniline process has been developed by the Standard Oil Co. of California,<sup>71</sup> but has not been put into commercial operation due to the poisonous nature of the solvent. The physical properties of aniline, ( $C_6H_5NH_2$ ), are given below.

TABLE 36—Physical Properties of Aniline

|                  |                 |
|------------------|-----------------|
| Molecular weight | 93.06           |
| Boiling point    | 184.4° C.       |
| Melting point    | — 6° C.         |
| Specific gravity | 1.022 at 20° C. |

In its solvent characteristics, aniline approaches those of furfural requiring relatively higher extraction temperatures than other solvents in refining a given type of oil. For this reason, its commercial utilization is rather attractive, if the danger of poisoning can be avoided in plant operations.

\* Ferris<sup>60</sup> uses sulfuric acid and clay after nitrobenzene extractions for manufacturing white oils.

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## Chapter XIII

### Mixed Solvents

The lack of solvent power or of the desired degree of selectivity in some of the selective solvents, as well as a realization of the advantages to be gained by increasing the flexibility of solvent extraction operations, resulted in the development of mixed solvents. In such mixtures, the component present in greatest amounts is usually referred to as "primary solvent," while the component employed to modify the characteristics of this primary solvent is referred to as "secondary" solvent. By properly selecting such components it is, evidently, possible to adjust the selectivity and the solvent power of the mixture to any desired temperature of extraction or to make necessary compensations for variations in the nature of the stock treated. For these reasons, it may be considered within certain limitations that the use of mixed solvents tends to eliminate the temperature variable in solvent refining operations.

Although mixed solvents generally contain only two components of the above mentioned type, in a few instances additional components may also be used for depressing some of the other undesirable characteristics of solvents such as high melting points, etc. As chemically pure compounds are frequently lacking in some of the properties required of ideal solvents, the use of solvent mixtures of one or of another type is by no means uncommon. The discussion below is restricted, however, to solvent mixtures which were developed for the purpose of improving the solvent characteristics of individual components as the improvement of their other properties makes the problem of specific and not of general importance.

#### Component Solvents

As previously stated, the primary solvent in such mixtures is considered the one present in greatest amount and possessing low selectivity or low solvent power within the desired range of extraction temperatures. The improvement of selectivity or solvent power is obtained by adding a secondary solvent which must possess high selectivity or high solvent power. It is always desirable when the solvent having high solvent power has also a good selectivity, which may be sometimes concealed by its high solvent power, although this is not always an absolute requirement, provided the selectivity of the other solvent is very high and is not excessively deteriorated by addition of the high solvent power solvent. In some

instances, the primary solvent may possess both high selectivity and high solvent power, and addition of the secondary solvent may have as its purpose the lowering of the solvent power of the primary solvent. This is illustrated by the use of phenol containing certain quantities of water or of lower alcohols, and by other similar combinations. Secondary solvents may be, therefore, also defined as substances added to the primary solvents for modifying their solvent power without deteriorating appreciably their selective solvent properties.

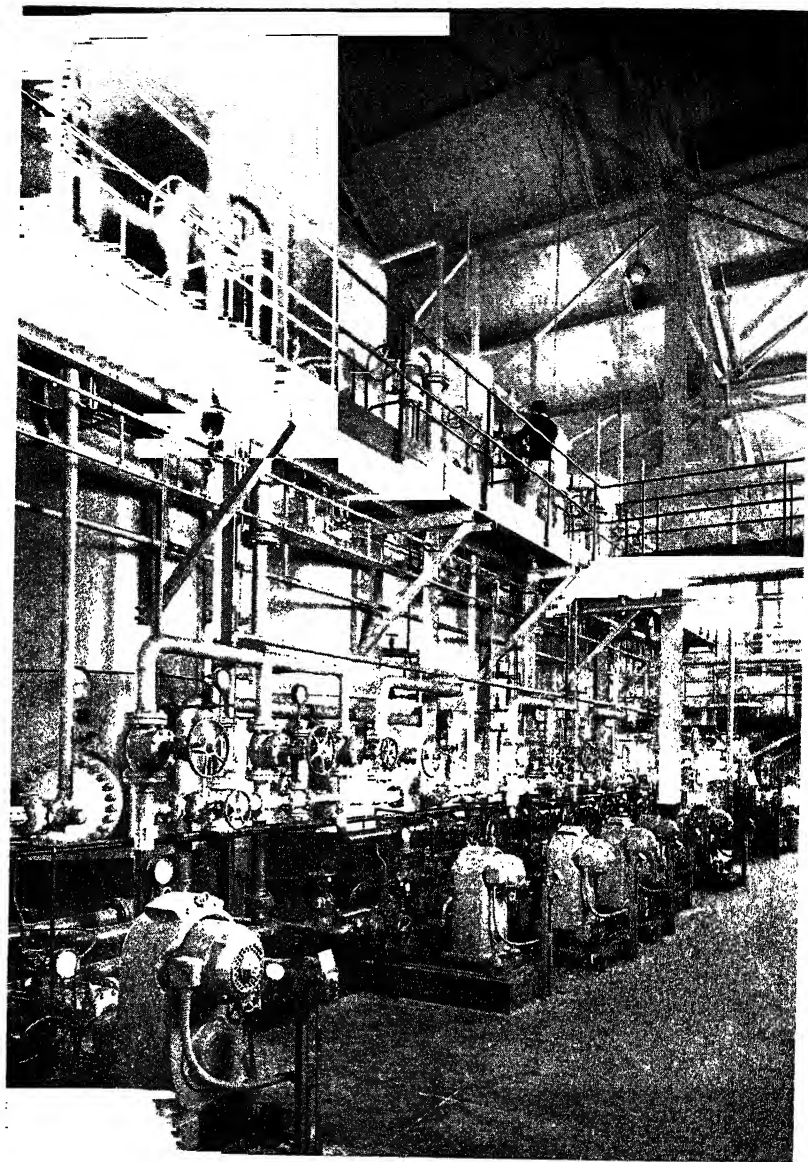
In using mixed solvents, it is frequently observed that for a given oil and temperature of extraction there exists an optimum quantity of the secondary solvent which may be employed for obtaining the most satisfactory results. This is obvious from the above discussion, as insufficient quantity of the secondary solvent results in the lack of solvent power of such mixtures, while excessive amounts may result in the loss of their selective solvent properties.

By varying the relative quantities of the components in a mixed solvent the miscibility region is sometimes reached by addition of a secondary solvent to the primary solvent at a constant temperature of extraction at the expense of the extract and not of the raffinate phase. The observed phenomenon is due to the gradual increase in the concentration of the secondary solvent in the raffinate phase which disturbs the equilibrium and increases the solubility of the primary solvent as well as of the previously extracted impurities in the raffinate phase.

### Mixed Solvent Processes

Commercial processes which are distinctly based on the use of solvent mixtures are, as yet, relatively few, but it is possible that they will become more numerous in the future because they introduce a variable in solvent refining operations which is capable of exercising certain control over other variables more difficult to adjust. Of the mixed solvent processes, the liquid sulfur dioxide-benzol process is successfully operated commercially, while the acrolein-crotonaldehyde process has passed the semi-commercial state of development. These two processes are described in greater detail below. The following combinations of solvents have also been proposed, however, some of which are in more or less limited use.

Mixtures of primary solvents comprising aromatic, heterocyclic, or aliphatic material and a secondary solvent consisting of ketones;<sup>1</sup> mixtures of a formate of a lower alcohol of the fatty series and an organic solvent having a greater solvent power for asphaltic bodies than the formate, such as benzol, carbon disulfide, carbon tetrachloride, etc.;<sup>2</sup> mixtures of acetone and a chlorinated aliphatic ether;<sup>3</sup> mixtures of chlorex and liquid sulfur dioxide;<sup>4</sup> mixtures of methanol and a low boiling hydroaromatic hydrocarbon;<sup>5</sup> mixtures of ethylene dichloride and methanol;<sup>6</sup> mixtures of chlorinated ether and gasoline;<sup>7</sup> mixtures of furfural and amylamine;<sup>8</sup> mixtures of methyl alcohol and phenol,<sup>9</sup> or of a polyhydric alcohol and



*Courtesy: Edelmann Company, Ltd.*

PLATE VII.—Benzol-Liquid Sulfur Dioxide Solvent Refining Unit.  
Mixing and settling tank equipment.

phenol;<sup>10</sup> mixtures of phenol with cyclic alcohols;<sup>11</sup> mixtures of phenol, furfural or aniline with organic solvents having specific gravity greater than one and which also have good solvent properties for asphaltic compounds such as ethylene dichloride, etc.;<sup>12</sup> mixtures of two solvents, one of which is solid and the other liquid at ordinary temperatures, such as phenol and cyclohexanol or cyclohexanone;<sup>13</sup> mixtures of furfural, furfuryl alcohol, aniline, phenol, methyl cellosolves, etc., with solvents having relatively low miscibility temperatures with the oil, such as cresylic acid, pyridine, benzaldehyde, nitrobenzene, nitrotoluene, benzonitrile, etc.;<sup>14</sup> mixtures of aromatic nitro compounds, xylinines, chlorobenzenes, chlorophenols, phenylacetates, halogenated ethers, heterocyclic compounds, such as dioxane, piperidine, furfural, thiophene, aldehydes or halogenated aliphatic hydrocarbons with ketones of low boiling point;<sup>15</sup> mixtures of furfural and naphthalene;<sup>16</sup> mixtures of furfural with benzol, toluol or light petroleum hydrocarbons, such as propane, butane, pentane, etc.;<sup>17</sup> mixtures of furfural and furfuryl acetate;<sup>18</sup> mixtures of phenol and tetrachloroethane;<sup>19</sup> mixtures of liquid carbon dioxide and sulfur dioxide;<sup>20</sup> mixtures of liquid sulfur dioxide and phenol;<sup>21</sup> mixtures of liquid sulfur trioxide and carbon dioxide;<sup>22</sup> mixtures of acetonitrile with benzol derivatives, heterocyclic compounds containing oxygen or nitrogen, such as phenol, cresols, cresylic acid, nitrobenzene, aniline, furfural, furfuryl alcohol, pyridine, aliphatic compounds containing nitrogen or chlorine, such as ethylene diamine, propylene dichloride, ethylene chlorohydrin, dichloroethyl ether, ethyl chloroacetate, or aliphatic compounds containing at least two oxygen atoms, such as monomethyl ether of ethylene glycol, glycol diacetate, methyl formate, vinyl esters, aliphatic alcohols, such as butyl alcohol, amyl alcohol, etc., cyclohexanol, aliphatic ketones, such as acetone, aliphatic aldehydes, such as crotonaldehyde, unsaturated aliphatic ethers, such as vinyl ethers of low molecular weight, and liquid sulfur dioxide;<sup>23</sup> mixtures of methyl alcohol with solvents having a greater solvent power for aromatic and naphthenic hydrocarbons;<sup>24</sup> mixtures of selective solvents with polycyclic aromatic hydrocarbons;<sup>25</sup> mixtures of liquid sulfur dioxide and nitrogen bases, such as quinoline;<sup>26</sup> mixtures of phenol and resorcinol or similar compounds;<sup>27</sup> mixtures of ethers and chlorinated ethers;<sup>28</sup> mixtures of acetone and triethanolamine;<sup>29</sup> etc. Obviously any solvent having more or less pronounced selective solvent characteristics might be employed for extraction purposes in combination with another similar solvent or with a solvent of an inert nature and for this reason, the number of possible combinations of solvents which are capable of separating petroleum oils into fractions is almost infinite. The number of patents of this nature can be, therefore, expected also to increase continually, although only a very few of them can be anticipated to be of exceptional practical value.

Only a few strictly mixed solvent processes are in use. However, single commercial solvents may be also regarded as mixtures because

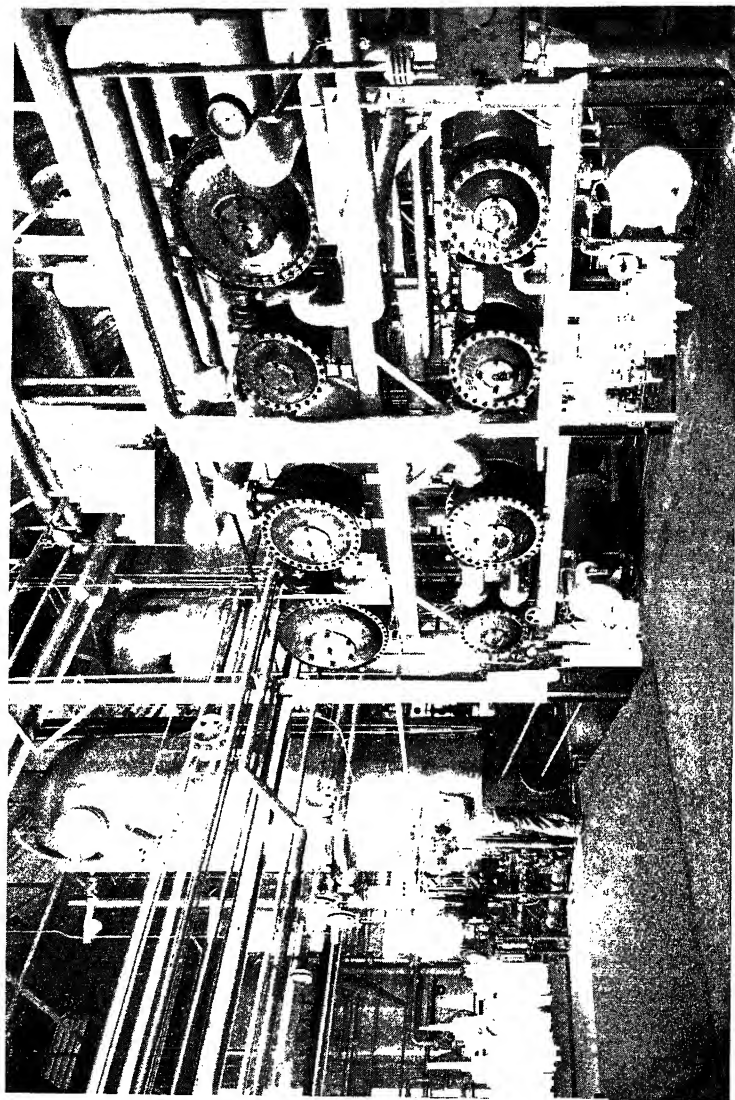


PLATE VIII.—Benzol-Liquid Sulfur Dioxide Solvent Refining Unit.  
Heat exchangers with sulfur dioxide treaters in the background.  
*Courtesy: Edleau Company, Ltd.*

their purification is not necessarily carried out to the extreme. The impurities which they contain should be regarded, however, as accidental and, for this reason, they cannot be considered as mixed solvents, although by rigid definition practically all of the commercial solvent processes employ mixed solvents.

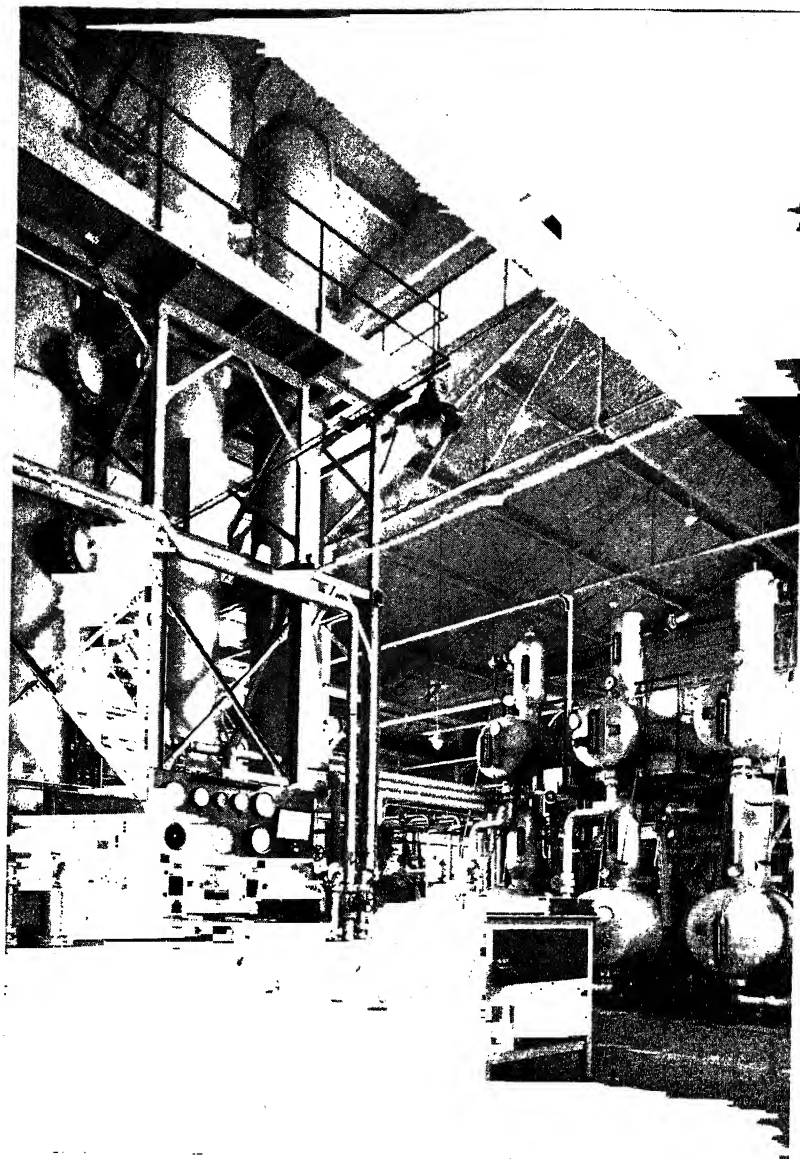
### Liquid Sulfur Dioxide—Benzol Process

Solutions of sulfur dioxide in various solvents have been recommended for a number of years as substitutes for the liquid sulfur dioxide of the Edeleanu process for treating oils. Saturated aqueous solutions of sulfur dioxide are entirely without action on simple olefins at ordinary temperatures, but diolefins give resinous polymers which contain sulfur.<sup>30</sup> Solid or semi-solid petroleum hydrocarbons are purified by treatment with a solution of sulfur dioxide dissolved in a solvent, the latter of which assists in the removal of the impurities from the oil. Solvents like acetone, alcohol,<sup>31</sup> or ketones and technical solvents obtained in the destructive distillation of wood<sup>32</sup> can be used. The treatment is carried out at ordinary temperatures, and the purified non-liquid products, such as paraffin, are separated from the liquid by filtration.<sup>33</sup> A solution of sulfur dioxide in acetone dissolves unsaturated hydrocarbons and resins, and can be used for the refining of oils or for absorbing gaseous olefinic hydrocarbons. The solvent, because of the low boiling points of the constituents, can be recovered from the extracted materials by distillation. Schmitt<sup>34</sup> points out that these mixed solvents, in contrast with the liquid sulfur dioxide, do not need pressure equipment.

The important commercial development in the Edeleanu process which made it applicable to the refining of lubricating oils appeared, however, only with the incorporation of benzol into the sulfur dioxide,<sup>35</sup> which improved the solvent properties of the liquid sulfur dioxide to an extent where the desired flexibility of the process was obtained within commercial temperature limits.

Mixtures of liquid sulfur dioxide with aromatic substances other than benzol are also recommended. Rutherford<sup>36</sup> uses mixtures of liquid sulfur dioxide with the substances extracted by the liquid sulfur dioxide from petroleum oils. Starr and Phillips<sup>37</sup> and Standard Oil Development Co.,<sup>38</sup> specify similar mixtures but extend them to solvents other than liquid sulfur dioxide, such as phenol, aniline, or furfural. Parkhurst<sup>39</sup> extracts lubricating oil stocks with mixtures of liquid sulfur dioxide and vapor-phase cracked naphtha containing at least 25% olefins. FitzSimons and Croxton<sup>40</sup> use solvent containing 20-95% liquid sulfur dioxide and liquefied olefins of two to five carbon atoms, such as propylene. Other combinations of liquid sulfur dioxide with various solvents were mentioned at the beginning of this chapter.

The quantity of benzol added to liquid sulfur dioxide for increasing its solvent power depends on the nature of the stock and the desired quality of the finished product. As the two solvents are recovered separately, no particular difficulty is encountered in adjusting the mixtures used in subsequent extractions. The plant resembles in general the plants used for



*Courtesy: Edeleanu Company, Ltd.*

PLATE IX.—Benzol-Liquid Sulfur Dioxide Solvent Refining Unit.  
Solvent recovery equipment and control panel.

straight sulfur dioxide extractions with the exception of having a more elaborate solvent recovery system. The process is now being successfully operated by several oil companies, including the Union Oil Co. of California.

### Crotonaldehyde Process

The process was developed by the Foster-Wheeler Co.,<sup>41</sup> but apparently has not yet been tried on a commercial scale. Originally, flexibility was obtained by employing mixtures of crotonaldehyde and acrolein adjusted so as to obtain the desired solvent effect on the oil. The properties of these two solvents are as follows:

TABLE 37—Properties of Crotonaldehyde and Acrolein

|                                     | Crotonaldehyde         | Acrolein             |
|-------------------------------------|------------------------|----------------------|
| Chemical formula                    | $C_3H_5CHO$            | $C_2H_3CHO$          |
| Molecular weight                    | 70.07                  | 56.05                |
| Boiling point                       | 218° F. (103.3° C.)    | 126.3° F. (52.4° C.) |
| Freezing point                      | -103° F. (-75° C.)     | .....                |
| Specific gravity at 68° F. (20° C.) | 0.859                  | .....                |
| Viscosity, centipoises at 85° F.    | 0.539                  | .....                |
| Viscosity, SUV 100° F.              | 31.5                   | .....                |
| Vapor pressure, mm.Hg. at 100° F.   | 80                     | .....                |
| Specific heat                       | 0.50 B. t. u./lb./° F. | .....                |
| Latent heat of vaporization         | 214 B. t. u./lb.       | .....                |
| Flash (closed cup)                  | 44° F.                 | .....                |

Both of these solvents are highly soluble in water. The use of centrifuges was recommended for the better separation of the two phases.

As a further development of this process, acrolein has been replaced by water. Crotonaldehyde dissolves from 9% to 10% of water at operating temperatures and, by varying its water content, the solvent may be adapted for the extraction of various lubricating oil stocks. The separation of crotonaldehyde from water is said to present no difficulties on the commercial scale.

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## Chapter XIV

### Double Solvents

The double solvent processes employ two solvents which have relatively low mutual solubilities and one of which has preferential solubility characteristics towards the undesirable oil constituents, while the other is claimed to have similar characteristics but towards the desirable oil constituents. These processes can be visualized as single solvent processes with the raffinate phase in solution in another solvent. This parallels, therefore, to a certain extent, refining of oils in naphtha solution with sulfuric acid, a process well known to petroleum refiners.

#### Paraffinic Solvents

The choice of a proper "paraffinic" solvent for the raffinate phase is somewhat difficult as not many solvents are available which, when mixed with oil, are capable of forming two phases within the desired temperature ranges after such solutions are brought in contact with the second or so-called "naphthenic" solvent. In practice, the paraffinic solvents are restricted to light aliphatic hydrocarbons as represented by propane and allied substances, while naphthenic solvents are likewise limited to a relatively few compounds satisfactory for extraction at atmospheric temperatures.

Although paraffinic solvents are generally considered to have preferential solvent action towards the desirable oil constituents, this is, apparently, open to question, particularly in the absence of asphalt. Thus, by extracting a Coastal distillate oil in naphtha solution with aniline, in which the naphtha was substantially immiscible, the yield and properties of the raffinate were found to be the same as those of the raffinate obtained by extracting the distillate with the same quantity of aniline in absence of naphtha. This does not preclude the possibility that by employing other solvents or other non-asphalt bearing oil stocks, dilution of the extracted oil with naphtha or allied substances may be beneficial. However, such a beneficial effect may also be explained by the effects associated with the extraction of impurities from more dilute solutions, to the reduction in the viscosity of the oil phase resulting in improved settling rates, etc., rather than to actual preferential solubility characteristics of the paraffinic solvents.

Bray, Swift, and Carr,<sup>1</sup> observed that the amount of selective solvent required to give a raffinate of a definite quality may be slightly greater when propane is

used, but that the benefits of increased yield and saving on subsequent treatment are often more than sufficient to justify the use of propane with a suitable solvent. This also indicates that the presence of the paraffinic solvent changes the selectivity and solvent power characteristics of the naphthenic solvent, which can be expected from general considerations based on the distribution law principles, rather than from additional assumptions about the special selectivity characteristics of paraffinic solvents.

When light hydrocarbon solvents, such as propane, are employed, however, for diluting the asphalt bearing oils, the asphalt is at least partially precipitated from such solutions due to the deasphalting characteristics of such solvents which were described in detail in previous chapters. The precipitated asphalt is thus forced into the naphthenic solvent in which it is soluble and which is likewise capable of extracting the low viscosity index and undesirable constituents of petroleum oils. As a result, the double solvent processes are in a degree capable of both deasphalting and solvent refining the asphalt bearing oils in one operation, which is frequently advantageous. Moreover, paraffinic solvents are, within certain limits, capable of dissolving some of the wax present in the oil, thus reducing the emulsification difficulties which are often encountered in extracting such wax bearing stocks with naphthenic solvents at temperatures at which the wax begins to crystallize.

In the above discussion, the assumption was made that paraffinic and naphthenic solvents are mutually immiscible, which is only approximately correct, as actually they are to a greater or less extent mutually soluble, and, at higher temperatures, even completely miscible. In presence of oil their mutual solubility characteristics are usually intensified or, at least, undergo further changes. The presence of the paraffinic solvent in the extract phase and of the naphthenic solvent in the raffinate phase likewise influences the distribution of the desirable and undesirable oil constituents between these two phases. The resulting system is, therefore, of such complexity that it can be studied only by empirical methods as applied to individual combinations of oils and solvents in which the refinery is particularly interested. The effect of these variables is further discussed in connection with the Duo-Sol process, which is described in more detail later.

From the foregoing discussion it follows that the extract from the double solvent processes contains both the asphaltic and low viscosity index constituents which can be separated from each other only with difficulty. These two oil components are recovered separately if the deasphalting and solvent refining operations are not combined into a single operation, and such segregation facilitates the utilization of these components for manufacturing various types of by-products. Likewise, as paraffinic solvents are also dewaxing solvents, their properties are not fully utilized. For these reasons, at some plants\* residual oils are first

\* Shell Oil Co. plant at Wood River, Ill.

deasphalted and dewaxed with propane and the resulting propane solution is then brought in contact with the naphthenic solvent.

Cresylic acid—phenol mixture, similar to that employed by the Duo-Sol process, described further below, is being used. Edeleanu Ges. m.b.H.,<sup>2</sup> specifies refining of oils first with light hydrocarbons, such as ethane, propane, butane or pentane, and then contacting the solution counter-currently with liquid sulfur dioxide, chlorex, nitrobenzene, furfural, or their mixtures with benzol or chloroform. See also Tuttle,<sup>3</sup> who treats the distillate oil with nitrobenzol or other solvents in presence of propane employing recycling operations.

### Double Solvent Processes

Of the commercial processes employing double solvents, the Duo-Sol process is of outstanding interest. The following combinations of solvents also have been proposed, however, although they are not yet applied to practice: propane or similar "paraffinic" solvents in combination with chlorex,<sup>4</sup> chloraniline,<sup>5</sup> liquid sulfur dioxide,<sup>6</sup> nitrobenzene,<sup>7</sup> phenol,<sup>8</sup> benzyl alcohol, furfural, nitrotoluene, aniline, pyridine, ethyl chloroacetate, cresol, wood tar acids,  $\alpha$ -naphthol, acetone, glycol diacetate, cellulose acetate, benzonitrile or nitrobenzene,<sup>9</sup> phosphates of a phenol,<sup>10</sup> etc., or "paraffinic" solvents of the type of aliphatic alcohols in combination with naphthenic solvents.<sup>11</sup>

### Duo-Sol Process

The process was developed by M. H. Tuttle of the Max. B. Miller Co., and is now successfully operated by several large oil companies.<sup>21</sup>

Tuttle<sup>12, 13</sup> specifies the use of wood tar acids, and the use of cresylic acid in combination with propane. The Max B. Miller Co. patents,<sup>14, 15</sup> cover the use of a combination of a paraffinic solvent (ethane, propane, butane, petroleum ether, gasoline, etc.) and a naphthenic solvent (cresol, guaiacol, or beechwood creosote); another British Patent<sup>16</sup> specifies extraction with a mixture of a liquefied normally gaseous hydrocarbon and a naphthenic solvent. Max B. Miller Co.,<sup>17</sup> specifies a paraffinic solvent such as propane and a naphthenic solvent such as nitrobenzene, nitrotoluene, benzyl alcohol, liquid sulfur dioxide, furfural, pyridine, or aniline. Max B. Miller Co.<sup>18</sup> specifies cresylic acid and a paraffinic solvent such as ethane, propane, butane, etc. Tuttle<sup>19, 20</sup> covers various operating details for double solvent processes.

In this process propane is employed as the paraffinic solvent and cresylic acid, usually containing from 20% to 40% phenol, as naphthenic solvent.

The use of cresylic acid as a single solvent is usually specified in most of the patents covering phenol and vice versa. Cresylic acid is specified as such by Katz,<sup>22</sup> Clarke<sup>23</sup> uses the extract derived from the soda washing of cracked distillates which is, evidently, composed of phenol and cresol-like hydroxy compounds. Burstin<sup>24</sup> finds that cresol is very effective in refining lubricating oils rich in paraffin as this permits the isolation of high grade asphalt free from wax, etc. In general cresylic acid might be characterized as a solvent of good selective properties but of high solvent power at normal operating temperatures being in this respect similar to nitrobenzol.

The properties of propane and phenol have already been described, while the properties of cresylic acid and allied substances are given below.

TABLE 38—Properties of Cresylic Acid and Cresol

|   | Cresylic Acid | Cresol<br>(mixture of<br><i>meta</i> - and <i>para</i> -) |
|---|---------------|---|
| Chemical formula                          | .....         | $C_6H_4(CH_3)(OH)$  |
| Molecular weight                          | .....         | 108.10  |
| Boiling point                             | 365–400° F.   | 396° F.   |
| Specific gravity at 68/68° F.             | 1.045         | 1.035   |
| Specific heat, B. t. u./lb./° F.          | 0.53          | 0.525   |
| Latent heat of vaporization, B. t. u./lb. | 180           | 178   |
| Flash point (closed cup)                  | .....         | 186° F.   |
| Boiling point at 100 mm.Hg.               | .....         | 281° F.   |

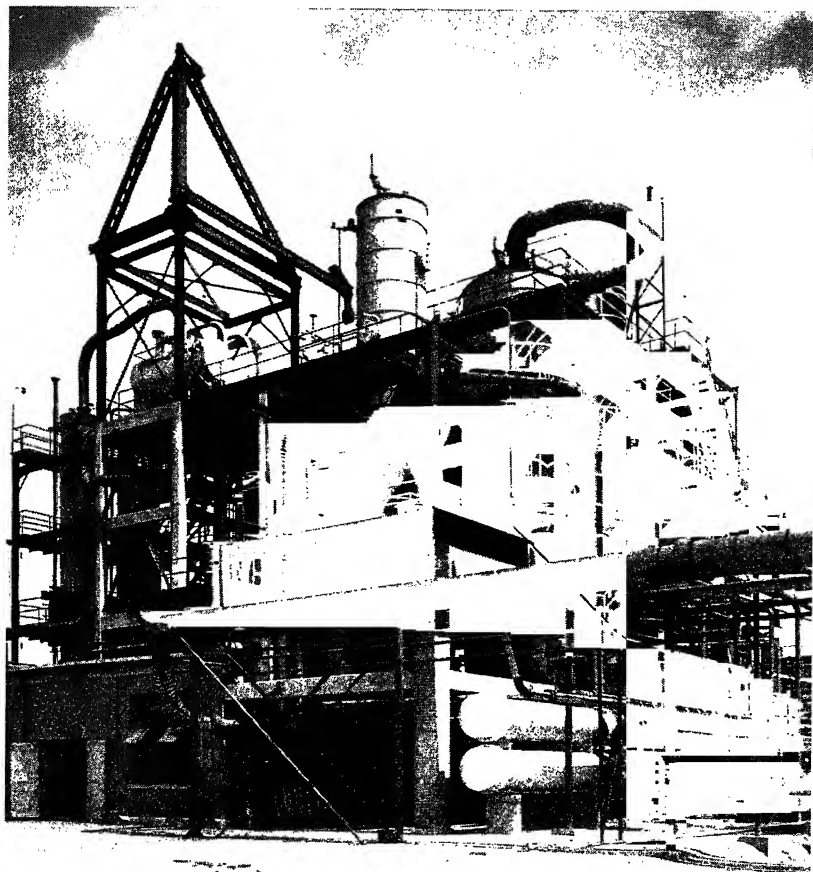
Propane acts as a deasphalting agent, and, therefore, the Duo-Sol process is intended to operate on oils which are not deasphalted, thus combining the deasphalting and solvent refining operations. Due to the dilution of oil with propane, the viscosity of the raffinate phase is low and its separation from the extract phase is usually relatively easy. Under the normal treating temperatures of 60° F. to 90° F. the solubility of wax in propane is sufficiently high with most stocks so as to permit the solvent extraction of most oils in the undewaxed state.

Propane, having a considerable solvent power towards the oily constituents, tends to remove the oil from the extract which explains the necessity of employing in combination with it a solvent of relatively high solvent power such as cresylic acid. If solvents of lower solvent power are used at the same temperatures, their effect is usually not sufficient for satisfactory refining or the quantity of solvent required becomes prohibitive.

Due to the high vapor pressure of propane, it is not desirable to use high treating temperatures as this would increase still further the cost of pressure equipment. Low temperatures are likewise to be avoided, particularly with wax-bearing stocks, due to the emulsification difficulties. The use of a mixture of phenol and cresylic acid for the "naphthenic" solvent permits, however, the adjustment of its composition so as to allow the extractions to be carried out within the desired temperature range. The propane present seems also to decrease the susceptibility of the solvent to temperature fluctuations as the decrease in yield with increase in treating temperature appears to be less for this combination of solvents than for other solvents, provided the number of extraction stages remains constant. The quality of product, at the same time, remains relatively constant over a considerable temperature range.

Due to the necessity of using two solvents, the total solvent to oil ratio is usually high, up to 400% of cresylic acid-phenol, and 400% by weight of propane being frequently required to obtain the desired products. Even larger ratios than the above mentioned are not uncommon.

The data below show the relative effects of varying propane-cresylic acid ratios in refining an overhead cylinder stock from a Coastal crude of



*Courtesy: Max B. Miller and Co., Inc.*

PLATE X.—Duo-Sol Solvent Refining Unit.

200 Saybolt Universal seconds at 210° F., about 20 viscosity index, and 2.3 carbon residue. Seven stage extractions were used in these experiments, in addition to two stages employed for removing oil from the extract layer, by washing it with fresh propane before this propane is employed for diluting the fresh oil charge.

TABLE 39—Duo-Sol Extractions of Coastal Distillate

| % Weight of Solvents Employed |         | Raffinate Yield<br>(% Volume) | Properties of Dewaxed Raffinate |                |                          |                   |
|-------------------------------|---------|-------------------------------|---------------------------------|----------------|--------------------------|-------------------|
| Cresylic Acid                 | Propane |                               | Viscosity Index                 | Carbon Residue | Color Lovibond (½" Cell) | S.U.V. at 210° F. |
| 150                           | 200     | 85                            | 60                              | 0.72           | 90                       | 135               |
| 150                           | 400     | 77                            | 58                              | 0.51           | 85                       | 129               |
| 400                           | 400     | 67                            | 82                              | 0.10           | 17                       | 102               |
| 600                           | 400     | 60                            | 83                              | 0.07           | 5                        | 99                |

The following data refer to similar extractions of a Mid-Continent residual stock of 150 Saybolt Universal seconds at 210° F., 70 viscosity index (after removing the wax, but before extracting with solvents), and 4.3 carbon residue after dewaxing.

TABLE 40—Duo-Sol Extractions of Mid-Continent Residuum

| % Weight of Solvents Employed |         | Raffinate Yield<br>(% Volume) | Properties of Dewaxed Raffinate |                |                          |                   |
|-------------------------------|---------|-------------------------------|---------------------------------|----------------|--------------------------|-------------------|
| Cresylic Acid                 | Propane |                               | Viscosity Index                 | Carbon Residue | Color Lovibond (½" Cell) | S.U.V. at 210° F. |
| 100                           | 200     | 86                            | 84                              | 1.1            | 525                      | 115               |
| 100                           | 600     | 90                            | 77                              | 1.0            | 260                      | 124               |
| 300                           | 200     | 74                            | 96                              | 0.5            | 325                      | 104               |
| 300                           | 600     | 81                            | 91                              | 0.5            | 165                      | 103               |

These data show that by keeping the propane-cresylic acid\* ratio constant and by increasing the solvent to oil ratios, raffinates of increasingly better viscosity index and carbon residue characteristics are obtained. By increasing the quantity of propane the viscosity index of the oil is somewhat lowered, while the carbon residue may or may not be improved. By increasing the quantity of cresylic acid, both the viscosity index and carbon residue are improved. The above data were presented with the primary object of illustrating the complex nature of the double solvent extraction system. In general, the Duo-Sol process is capable of refining oils from different crudes with a greater degree of flexibility than other solvent refining processes, although it may be somewhat less flexible in producing oils of different characteristics from a given type of crude.

In commercial operation the fresh oil is introduced two stages from the extract exiting end of a nine stage system with the propane and the cresol-phenol mixture at the extract and raffinate outgoing stages, respectively.

\* Mixtures containing 60% cresylic acid and 40% phenol were actually used.

### Sulfuric Acid Refining in Propane Solution

The advantages and disadvantages of sulfuric acid refining lubricating oil stocks in naphtha solution are well known.<sup>25</sup> In general, by treating in light diluent, the yields as well as the quality of the resulting products are considerably improved due to the ability of more effectively separating the sludge from the oil at low treating temperatures, which are, in general, preferable in sulfuric acid refining. However, the possibility of discoloring the oil in removing naphtha by distillation should not be overlooked.

The substitution of propane for naphtha is, therefore, a logical development of the above processes. Besides having all of the desirable characteristics of naphtha, propane can be removed from the oil without the use of excessive distillation temperatures, and by being a rather powerful deasphalting agent it intensifies still further the action of sulfuric acid, thus reducing the acid consumption for a given degree of improvement in oil properties. Furthermore, propane is capable of keeping the whole body of the oil at a constant temperature during the acid treat, as the heat generated in such treats is easily dissipated through vaporization of propane, the temperature of which is controlled by pressure. This permits application of acid in one portion instead of dividing it into several portions, which is now a common practice. Wilson, Keith, and Haylett<sup>26</sup> state that the combined effect of the above variables may result in a saving of as much as 80% of sulfuric acid when the oil is treated in propane solution as compared with treatment in the undiluted state. The yield of the finished oil is likewise increased. A commercial plant of the above type is now being operated by the Standard Oil Co. of Indiana on a Mid-Continent residuum. A series of patents have been issued for refining oils with sulfuric acid in propane solution.<sup>27</sup>

The sulfuric acid refining can be also used in combination with solvents for deasphalting purposes. The oil is first diluted with propane and then treated with sulfuric acid and liquid sulfur dioxide,<sup>28</sup> or with liquid sulfur dioxide and then with sulfuric acid.<sup>29, 30</sup> According to Garofalo,<sup>31</sup> the oil can be also diluted with propane, treated with sulfuric acid and chilled by evaporating some of the propane for simultaneously separating sludge and wax.

Refining of lubricating oils with clays in presence of propane is claimed to give also highly satisfactory results. Such contacts are, evidently, made at temperatures which are comparatively low, due to high pressure of propane. However, by contacting at 160-170° F., the efficiency of clays is claimed to be improved by as much as 300-400% in presence of propane, due to its additional deasphalting action.

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## Chapter XV

### Disposal of Solvent Extracts

In view of the rapid growth of the solvent extraction processes the problem of disposing of the solvent extracts becomes of increasing commercial importance. The extracts from solvent refining obviously contain those constituents of the raw petroleum fractions, which are characterized by a low viscosity index, high carbon residue, and considerable chemical reactivity. The extracts are free, however, of paraffin wax, except for small quantities of it which are often introduced into the extracts by mechanical entrainment in treating the wax bearing stocks. The extracts differ from the sulfuric acid sludges, the common waste material from the conventional sulfuric acid treating processes, in being free from sulfonated materials, and this fact greatly facilitates their handling and their utilization around the plant.

Chemically, the extracts may be regarded as being composed of asphaltic and resinous bodies, substances of predominantly aromatic nature, and compounds of sulfur and nitrogen. The nature and appearance of these extracts vary with the nature of the processed crude, its preliminary refining, viscosity of the treated fraction, and the severity and completeness of the solvent treat. In contrast with sulfuric acid, solvents have no chemical action on the oil, and extracts are, therefore, free of compounds formed in the course of refining, unless traces of such compounds are introduced by employing solvents which slightly decompose on distillation. This occurs, however, only when the conditions for distilling off the solvents from the oil are not sufficiently well worked out or when the distillation system becomes unbalanced.

In general, three types of extracts are available at the refineries: those from the deasphalting processes which contain primarily the asphaltic constituents, those from the solvent refining of deasphalted stocks which are practically free of asphalt but contain the low viscosity index constituents that are usually very reactive, and those from the double solvent processes, which contain both asphalt and low viscosity index constituents. The first two types of extracts are simpler to dispose of than the latter type which, unless used as fuel or as an admixture to asphalt, must be first separated into the asphaltic bodies and oil before they can be used as raw materials for further reworking into valuable by-products.

As all of the extracts depend, with respect to their actual chemical

composition, on the type of crude from which the oil is obtained, their utilization is likewise an individual refinery problem. While all of them obviously can be utilized as fuel, some of the more valuable extracts can be employed as raw materials for manufacturing more valuable by-products thereby increasing the returns of the refinery. Considerable amount of research has been conducted along these lines and, apparently, with better success than with the sulfuric acid sludges which, with a few exceptions, continue to remain a nuisance of the petroleum industry.

The huge quantities of solvent extracts now being obtained by the refineries involve the problem of their disposal in bulk quantities. The chemical nature of many of these extracts, however, suggests their utilization in a more efficient way as raw materials for various synthetic chemicals, but only a negligible portion of the extracts can be disposed in such profitable way. For this reason the discussion below is separated into two portions: disposal of the solvent extracts in bulk quantities and their reworking into various by-products of a more limited type.

Waste products from the deasphalting processes or the extracts from the double solvent refining processes which contain large quantities of asphalt might be frequently utilized in the manufacture of asphalts and road oils.<sup>1</sup> This frequently results in improved products with respect to ductility although the presence of excessive quantities of oil in the extracts may sometimes be harmful. For this reason, the quantity of extracts to be utilized in this way depends on the particular use for which such products are intended.

In refining lubricating oils to high grade products the extracts frequently contain fairly large quantities of relatively high viscosity index oils, which can be removed from the extracts by reextracting them again with solvents,<sup>2</sup> or by removing some of the solvent, or by chilling, or by adding an oil anti-solvent such as water or alcohol.

Reextractions with solvents should be, evidently, made under different treating conditions from the original extractions from which these extracts were obtained. The resulting products usually possess a fair degree of chemical stability while their viscosity index may frequently be equal to that of the oils formerly obtained from the Mid-Continent crudes by the conventional acid treating methods. For this reason, they can be disposed of as secondary grades of lubricating oils for which there is always a good market.

The possibility of recovering such second grade oils by reextracting the solvent extracts with solvents under modified conditions of extraction was discussed in Chapter XI where it was shown that considerable quantities of reasonably satisfactory oils may be obtained in this manner. As a modification of such methods it has been also proposed before separating the solvent to saturate the extract phase with water which displaces the oil from its solution in the solvent with a sufficient degree of

selectivity to obtain satisfactory products. The process of Suida is in this connection of some interest.<sup>3</sup>

In this process mixtures of cresol and nitrobenzene are employed for solvent refining and the extract is then saturated with water in order to expel additional quantities of second grade oils which are collected separately.<sup>4</sup>

Centrifugal separation of the two layers is resorted to in order to increase the rate of settling. The use of a mixture of nitrobenzene and cresol is explained as water is practically insoluble in nitrobenzene while its solubility in cresol is relatively high. A mixture of the two solvents can be therefore adjusted so that by saturating the extracts with water only the more valuable oil fractions are recovered from the extracts. These second grade oils are evidently always inferior to the originally recovered raffinates. The process is not applicable, however, to extracts containing appreciable quantities of hard asphalt as the hard asphalt is partially expelled by the water with the oil fractions and the resulting product has, therefore, a very high carbon residue and dark color which makes necessary a subsequent deasphalting operation before the product can be made of marketable value.

In evaluating the value of such processes, however, it should be always remembered that the relative yields of first and second grade oils depend on the sharpness of the solvent separation in primary extractions. The larger the quantity of valuable oils left in the extract, the higher will be the yield of the second quality product. The yield of this product can be, therefore, increased by decreasing the number of extraction stages in primary extractions or by changing other variables discussed in Chapter XII which control the amount of high grade oils lost to the extract phase.

The solvent extracts can be also improved by treating them with aluminum chloride,<sup>5</sup> whenever this is feasible. The process may not be necessarily applicable, however, to all the refineries, particularly to those which do not use the aluminum chloride process for oil refining.

With some extracts, particularly those from Pennsylvania type of oils, it is often possible to obtain fair looking products by merely treating them with clay or with sulfuric acid and clay. Such products, however, are usually unstable and have a low viscosity index, although they have all appearances of a high grade Pennsylvania oil. They cannot be marketed by any reputable oil company, but apparently some products of this type are being sold by small irresponsible concerns to the detriment of the consumer.

The extracts can be also hydrogenated, used as cracking stocks, or employed for the production of aromatic hydrocarbons.<sup>6</sup>

Their hydrogenation may be of commercial value only in refineries which are equipped with such expensive installations, but cracking them to gasoline is of greater importance since due to the aromatic nature of

the extracts they are capable of yielding high octane number cracked gasolines. However, as is observed on cracking crudes rich in aromatic compounds, coke formation may be excessive while gasoline yield will be relatively low.<sup>7</sup>

A large proportion of the solvent extracts is utilized as fuel oil.<sup>6</sup> It is to be hoped, however, that this practice will gradually diminish as new outlets are found for a more efficient utilization of these extracts. When used as fuel, the extracts, due to their aromatic nature, are frequently of value when used in blends with fuel oils from cracking processes which have a tendency to deposit sediment in storage. This sediment is formed due to the relatively poor solubility of the polymerized bodies in the more paraffinic oils, whereas solubility of such polymerized bodies becomes fair in blends of extract oils, which contain aromatic types of hydrocarbons. For this reason, addition of certain types of solvent extracts to cracked residuums may find commercial application for stabilizing the product.<sup>8</sup>

Limited quantities of extracts can also be employed as froth-flotation agents, for manufacturing certain types of gear oils, industrial lubricants, greases, etc., whenever the stability of the oil employed is of secondary importance. This, evidently, can be decided only by knowing the particular application for which the products are intended.

Considerable amount of work has been carried out on the possible utilization of solvent extracts for manufacturing different chemical by-products. Many helpful suggestions in this respect can be found in the fundamental work of Ellis<sup>9</sup> on the utilization of various petroleum products for the manufacture of chemicals.

A complete description of these methods is beyond the scope of the present work as it enters well into the field of organic chemistry. In general, however, it has been proposed to utilize the solvent extracts for the manufacture of resins, sulfonic acids,<sup>10</sup> dyes and pour point depressants,<sup>11</sup> etc. The manufacture of sulfonic acids appears in this respect to be attractive because the supply of sulfonates from the conventional sulfuric acid processes will diminish as the solvent refining processes become more and more universally adopted to the various needs of the petroleum industry.

It has been also proposed to use the solvent extracts for resolving crude oil emulsions.\* The chemical reactivity of extracts suggests their use for manufacturing oxygenated compounds by careful oxidation by air or oxygen, or by the sulfuric acid method.<sup>13</sup>

To recover the fluorescent matter from the extracts for artificial coloring of motor oils,<sup>14</sup> as well as to utilize the various nitrogen compounds if such are present in the extracts, has also been recommended.<sup>15</sup>

\* De Groote and Monson<sup>12</sup> recommend for this purpose the fraction of the extract which boils between 360° F. to over 490° F., and which is, therefore, obtained from products of the type of kerosene.

It should be expected that future research will reveal further possibilities for a profitable disposal of extracts from solvent refining as they present fewer difficulties than the sulfuric acid sludges when used as raw basic materials for further synthesis. To a great extent this will depend on the future trend of the petroleum industry which, in all probability, will gradually approach the status of other chemical industries where the recovery of by-products frequently determines the commercial utility of a given process.

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## Chapter XVI

### Pour Point Depressants

Improvement in lubricating oil quality may be accomplished not only by removing the undesirable constituents but also by adding to the oil various protective agents or other substances capable of improving service characteristics of natural products. The most important substances of this type are pour point depressants, oiliness carriers and extreme pressure materials, viscosity index improvers, oxidation inhibitors, and color improvers. Other similar materials are fillers, as represented by aluminum soaps used for manufacturing chatter proof lubricants, and diluents or light viscosity and low boiling point substances added to lubricating oils in order to eliminate some of the difficulties encountered in employing fresh oils before they become diluted with the heavy gasoline ends and attain normal viscosity in service. At the present time, however, the use of fillers is no longer warranted due to mechanical improvements in engines, while the use of diluents is likewise falling into disuse because corresponding improvements in the engine design and in the distillation characteristics of fuels have practically eliminated the dilution problem in operation of the modern internal combustion engines.

#### Effect of Wax on Oil Properties

It has previously been shown that the presence of wax in lubricating oils is undesirable for the main reason that wax bearing oils have a high congealing temperature resulting in an unsatisfactory circulation of such oils in the engine. If such circulation can be established, however, the engine performance depends primarily on the true viscosity of the oil and not on the pour point.<sup>1</sup> At temperatures at which the wax goes completely into oil solution, its presence may be even beneficial as, according to Davis and Blackwood,<sup>2, 4</sup> the presence of wax in oils increases the viscosity index, lowers the carbon forming tendency, improves volatility and oiliness, and raises the stability of oils towards oxidation.\*

The improvement in the viscosity index of an oil due to presence of wax is explained by the very low viscosity of the wax in a molten state. The effect of wax on the viscosity index is, therefore, the same

\* Standard Oil Development Co.<sup>3</sup> recommends improving service characteristics of lubricating oils deficient in wax, by adding to such oils some of the wax with the required amount of pour-point depressants to off-set the rise in the pour point.

as that associated with dilution of oils with low viscosity materials which has been discussed in Chapter I. Such improvement in the viscosity index is observed, however, only when wax is completely soluble in the oil at temperatures at which viscosities are measured, *i.e.*, at 100° F. and 210° F. employed in calculating viscosity indexes. If, however, wax dissolves completely in the oil at 210° F. while at 100° F. its solubility is incomplete, the viscosity index of such oil-wax blends is often inferior to that of the dewaxed oil. The effect of the presence of wax on the carbon residue of the oil has also been explained as being a dilution phenomenon because the carbon residue of wax might be considered as being nil. The effect of wax on volatility of oils as measured by flash and fire tests and on their oiliness is usually insignificant and may be even open to question, while its effect on oxidation characteristics depends to a great extent on the type of oxidation test employed and might be shown to be in either direction.

The effect of adding a pour point depressant (Paraflow), to wax bearing lubricating oils can be visualized from the following experimental data, given by Davis and Blackwood.<sup>4</sup>

TABLE 41—Effect of Adding Pour Point Depressant

| Properties               | Grade of Motor Oil |                           |       |                           |
|--------------------------|--------------------|---------------------------|-------|---------------------------|
|                          | As is              | S.A.E. 10<br>+1% Paraflow | As is | S.A.E. 30<br>+1% Paraflow |
| Gravity, ° A.P.I.        | 30.6               | 30.4                      | 27.4  | 27.5                      |
| S.U.V. at 100° F.        | 150                | 161                       | 481   | 474                       |
| S.U.V. at 210° F.        | 43.2               | 44.3                      | 62.3  | 62.0                      |
| Viscosity index          | 90                 | 99                        | 96    | 97                        |
| Pour point, ° F.         | +30                | -10                       | +30   | -10                       |
| Flash point, ° F.        | 380                | 395                       | 415   | 415                       |
| Carbon residue           | 0.014              | 0.055                     | 0.815 | 0.829                     |
| Color, Tag-Robinson      | 11                 | 10                        | 2½    | 2                         |
| Cloud point, ° F.        | 52                 | 46                        | 1620  | 1620                      |
| Demulsibility at 130° F. | 1620               | 1620                      | 1620  | 1620                      |

Summarizing the above effects of wax on oil properties it is apparent that its presence in the oil is at least not objectionable if the fluidity of the oil can be maintained at low temperatures. By leaving wax in the oil, however, the considerable expense of dewaxing operations can be eliminated to a certain extent while the yield of the oil is improved by the amount of wax left in the oil.

### Natural Pour Point Depressants

The possibility of discovering substances which are capable of lowering the pour point of oils has been indicated by the effect of some of the oil constituents on the fluidity of wax-bearing stocks at low temperatures. These constituents, which are of the asphaltic type, are removed from the oil in the course of deasphalting or solvent refining operations because their presence in finished products is objectionable due to their instability.

They can be isolated, however, by a variety of methods, for instance, by percolating unrefined petroleum residua through clay and by displacing the absorbed materials with various solvents. Fractions obtained from such filters, on washing with naphtha, appear very similar to the last portions of the oil passed through the filter. Fractions obtained by subsequently washing the filters with benzol are, in contrast, resinous in character, but their pour point depressant qualities are practically absent. However, materials removed from the filters by further washing with alcohols or similar solvents exhibit distinct pour point depressant characteristics.<sup>5</sup> Substances of similar nature can be also isolated by employing liquid precipitants such as low molecular weight hydrocarbons,\* or aliphatic alcohols.† Unfortunately, however, the quantity of such substances required for effecting the lowering of the pour point of the oil is rather large (several per cent) and when added in the required amounts they have an unfavorable effect on other oil properties, such as carbon residue, oxidation stability, and color. Similar difficulties are also encountered in employing pour point depressants obtained directly from such materials as cracking still or distillation residues,<sup>10</sup> hydrogenated tars from cracking processes,<sup>11</sup> tar pitch,<sup>12</sup> oxidized waxy hydrocarbons,<sup>13</sup> wax tailings,<sup>14</sup> etc.

### Synthetic Pour Point Depressants

Such inadequacies of natural inhibitors resulted in numerous attempts at synthesizing various compounds which, when added to the oil, would possess good pour point depressant qualities without unfavorably affecting other desirable oil properties. The recommended substances include benzyl chloride,<sup>15</sup> zinc or magnesium salts of acidic products derived from oxidation of paraffin wax,<sup>16</sup> aluminum stearate,<sup>17‡</sup> zinc or magnesium hydrostearates,<sup>20</sup> xylolstearamide,<sup>21</sup> distearyl naphthalene, dimyricyl ether of 1,5-dioxynaphthalene, cerotic acid, esters of cholesterol, or similar substances,<sup>22</sup> condensation products obtained by subjecting paraffin wax to silent high-frequency electric discharges,<sup>23</sup> or by subjecting to a similar treatment hydrocarbons containing from ten to twelve carbon atoms, esters, ethers, acids, ketones, etc.,<sup>24</sup> polymerization products of a vinyl ether of an unsaturated alcohol such as that of oleic alcohol,<sup>25</sup> substances obtained from wool fat,<sup>26</sup> condensation

\* Moser<sup>6, 7</sup> separates pour point depressants from pyrogenous condensation products by precipitation with aliphatic solvents, and employs a similar method for separating such substances from solvent extracts after heating the extracts to 350° C. (662° F.) for increasing their asphaltene content. See also Winning and Fulton.<sup>9</sup>

† Sloane<sup>9</sup> concentrates pour point depressants by extraction with butyl or amyl alcohols.

‡ Kaladzhali<sup>18</sup> finds that addition of aluminum stearate creates in some instances a "maximum" and a "minimum" pour point which can be eliminated by addition of triethanolamine. Barth and Corlew<sup>19</sup> specify aluminum salts of organic acids produced by the oxidation of paraffin wax.

products derived from a sugar having at least one cyclic nucleus and not more than two mono-saccharide groups in its molecule and an aliphatic acid, such as those of sucrose and stearic acid,<sup>27</sup> esterified hydrostearic acid,<sup>28</sup> aluminum soaps,<sup>29</sup> polystyrol, polyindene, hydrogenated natural or synthetic rubber or similar hydrocarbon polymerization products,<sup>30</sup> oxygenated vinyl compounds,<sup>31</sup> ethylene glycol distearate,<sup>32</sup> aluminum chloride condensation product of a higher fatty acid chloride, such as stearyl chloride, and a coal tar material,<sup>33</sup> mixed ketones,<sup>34</sup> condensation products of hydrocarbons rich in paraffin,<sup>35</sup> tristearate of pyrogallol and similar compounds,<sup>36</sup> glycerol tristearate,<sup>37</sup> esters formed from an alcohol containing at least ten carbon atoms,<sup>38</sup> rufigallic acid hexastearate, pyrogallol tristearate, resorcinol distearate and allied substances,<sup>39</sup> soaps of carboxylic acid containing more than nine carbon atoms and a metal of the titanium subgroup of Group IV of the Periodic System, such as titanium stearate,<sup>40</sup> nonparaffinic natural waxes, such as beeswax, spermaceti, myrica, candelilla, carnauba, china or lignite wax,<sup>41</sup> condensation products of a halide of an aliphatic organic compound having a long paraffin chain, such as chlorinated paraffin wax, and a monochloronaphthalene or bromophenol, followed by further condensation with sodium for removing the halogen atoms,<sup>42</sup> condensation products of oleic acid, a dichloroparaffin, such as ethylene dichloride, and an unsubstituted aromatic hydrocarbon,<sup>43</sup> condensation products of high molecular aliphatic hydrocarbons and aromatic compounds containing oxygen, such as condensation products of diphenylene oxide and chlorinated paraffin,<sup>44</sup> products obtained by heating chlorinated aliphatic hydrocarbons with an aromatic hydrocarbon,<sup>45</sup> organic compounds having one or more five or six membered rings with at least two side chains of ten or more carbon atoms, such as tristearate of pyrogallol acid or distearate of alizarine,<sup>46</sup> condensation products of an aromatic hydrocarbon material, such as naphthalene, and aliphatic hydrocarbon material, such as paraffin or monochlorowax, further condensed with a resinifying agent such as trioxymethylene,<sup>47</sup> etc.\*

The above list does not include patents which were issued in connection with the two best known commercial pour point depressants "Paraflow" and "Santopour" discussed in more detail on subsequent pages.

### Limitations of Pour Point Determinations

The effectiveness of the pour point depressants is usually measured by the lowering of the pour test of the oil. In carrying out such measurements the limitations of the test should be well understood. Both the pour and cloud tests of an oil depend on the size, form and rate of

\* Byers<sup>48</sup> gives a survey of the patent literature on pour point inhibitors showing that such substances had already been recommended for improving the fluidity of oils as early as in 1867. A total of 77 patents is abstracted.

formation of the wax crystals which, in their turn, frequently depend on the previous history of the sample. In order to eliminate the latter variable the sample is preheated to a relatively high temperature before starting the test in order to bring the wax crystals completely into oil solution.

Sachanen<sup>49</sup> observed that the solidification temperature of oils varies with the temperature to which the samples were heated, and that higher preheating temperatures depress solidification point which rises, however, to its original value in storage. Chernozhukov and Gutzait<sup>50</sup> recommend heating the oil to 212° F. (100° C.), in order to eliminate the effect of previous treatments. Woog, Ganster, and Coulon,<sup>51, 52</sup> find that if the oil is initially cooled at a very slow rate to -121° F. (-85° C.), and then reheated the melting point is at its maximum while rapid cooling does not give sufficient time for formation of the wax crystals.

Heating the oil before testing may cause a change not only in the pour test of the oil but also in its specific gravity and viscosity. These three attributes may be raised or lowered by preheating the samples, depending on whether cooling takes place with the oil at rest or in motion. They are raised or remain unaltered if cooling is accompanied by stirring and lowered if the cooled sample is held at rest. Investigation of the crystal structure of separated wax particles substantiates the conclusion that these differences should be attributed to the differences in the size and quantities of the wax crystals present.<sup>53</sup> While the above phenomena are not unusual with oils of Pennsylvania type,<sup>54</sup> they are also observed with Mid-Continent oils which contain both wax and asphalt.

An interesting observation of Moerbeek and van Beest<sup>55</sup> on the sensitivity of pour points to the thermal history of fuel oils showed that addition of small percentages of asphaltenes, precipitated from residual fuels by pentane, to a residual fuel oil, the pour point of which was insensitive to the temperature of pretreatment, improved the sensitivity of this fuel to the pour test. On the other hand, removal of asphaltenes from fuel oils, which are in themselves temperature sensitive as to their pour points, made them insensitive to temperatures of pretreatment.

It is well known that distillate fuels are, in general, not temperature sensitive with respect to their A. S. T. M. pour test, while residual fuels often give different results when preheated to different temperatures.

The pour test of an oil with or without addition of a pour point depressant, may in certain instances show no difference when the samples are tested by following the standard procedure,<sup>56</sup> while on slow chilling, samples containing the pour point depressant may show a considerably lower pour test.<sup>57</sup> Likewise oil samples, particularly those containing pour point depressants or very high melting point waxes, may show a low cloud test when tested under standard conditions, while on slow chilling or on standing at relatively low temperatures for a certain length of time, they may develop a cloud due to separation of wax at higher temperatures than those which can be predicted from the cloud test.

The use of pour point depressants in lubricating oils and the general characteristics of such products are discussed in detail in connection with the description of Paraflow, one of the commercial products which is now being marketed on a large scale. The discussion below is, therefore, applicable also to other pour point depressants besides Paraflow.

### Paraflow

Paraflow is a condensation product of chlorinated wax and naphthalene in presence of aluminum chloride.<sup>58</sup> It is marketed in oil solution which permits careful adjustment of the pour point depressant qualities of current production by varying the amount of oil used as diluent. When added in small quantities to the oil, such as 0.5% or less, it effectively lowers the pour point without unfavorable effect on other oil properties. If, however, Paraflow is added in large quantities, such as 2% or more, it may increase the carbon residue of the oil and the rate of carbon formation in the engine.<sup>59</sup> Its effectiveness can sometimes be improved if the oil has been previously well refined from asphaltic and resinous impurities.<sup>60</sup> This, however, is of secondary importance as Paraflow is practically always added to oils after they have been subjected to the various treating procedures. It should be noted, also, that oils containing Paraflow should not be further refined, because Paraflow may be removed from the oil in these operations, for instance, by percolation through clay.

Paraflow is usually added to oils which have been already dewaxed to a relatively low pour test, such as 20-25° F. in order to lower the pour test still further, to 0°F. or less. The use of Paraflow under these conditions permits the refiner to eliminate the necessity of using low refrigerating temperatures and to avoid two dewaxing operations which are sometimes needed if conventional dewaxing methods are employed for attaining such low pour tests.

Doladugin, Solodovnik, and Englin<sup>61</sup> observed that addition of Paraflow to Grozny mixed-base products containing 2-5% of paraffin wax has no effect on their pour points. They believe that the medium holding the wax in solution has a considerable effect on the behavior of Paraflow and that oils containing aromatic compounds of high freezing point are least affected by such additions.

In general, effectiveness of Paraflow decreases with the increase in viscosity of the oil. Exceptions to this rule are known, however, and occasionally a residual oil is found which responds to the addition of Paraflow and a distillate stock of relatively low viscosity which is relatively inert to such addition. Apparently, however, Paraflow is most effective with the paraffin and not with the ceresin type of waxes, and the lower the melting point of the wax, the more efficient is the action of Paraflow.<sup>59, 62</sup>

It is of interest that Paraflow itself has a relatively high pour point and, for this reason, addition of Paraflow to a wax free distillate may

actually result in an increase in the pour point of such oil. Addition of Paraflow to a wax bearing stock may likewise first lower the pour point and then raise it after the quantity of Paraflow added reaches an optimum. This is observed, however, only when very high quantities of Paraflow are added to the oil, which never occurs in commercial practice. The above behavior of Paraflow is illustrated by the following examples obtained with Coastal and Mid-Continent distillate stocks of 58 and 140 Saybolt Universal seconds at 100° F., respectively.

TABLE 42—Effect on Pour Point of Addition of Paraflow

| Paraflow<br>% Volume in Blend | Pour Point, ° F.   |                          |
|-------------------------------|--------------------|--------------------------|
|                               | Coastal Distillate | Mid-Continent Distillate |
| 0                             | — 70               | + 10                     |
| 3                             | — 65               | — 25                     |
| 5                             | — 60               | — 50                     |
| 10                            | — 55               | — 40                     |
| 20                            | — 50               | — 30                     |
| 30                            | — 40               | — 20                     |
| 50                            | — 25               | — 5                      |
| 80                            | — 5                | + 5                      |
| 90                            | + 10               | + 10                     |
| 100                           | + 20               | + 20                     |

The above tabulation shows, therefore, that, while Paraflow lowers the pour point of the wax bearing oil, such an oil is also capable of lowering the pour point of Paraflow.

It is generally agreed that the action of paraflow is due to its ability of inhibiting the excessive growth of the wax crystals and of changing their shape from the needle type to small equiaxial grains of uniform size.<sup>63</sup> Such small wax crystals do not interfere to any great extent with the flow of the oil but they are still able to develop a high cloud point. For this reason, although the pour point is reduced by Paraflow, the cloud point of the oil is affected to a considerably less degree, particularly, when the oil contains high melting point waxes.<sup>59</sup> In certain instances the differential between the pour and cloud points of an oil treated with Paraflow may become as high as 50-60° F., particularly with the Coastal type of stocks containing small quantities of high melting point waxes.

Paraflow is now being used almost exclusively for lowering the pour point of motor oils although it may find applications also in lowering the pour point of other petroleum products. The use of Paraflow in specialized oils of transformer or turbine type has not been found desirable, however, due to its unfavorable effect on some of their desirable characteristics, particularly, oxidation stability.<sup>59</sup>

### Santopour

This pour point depressant, which recently appeared on the market, has already found rather wide recognition in the petroleum industry. It

is obtained by condensing phenol and chlorinated wax in presence of aluminum chloride followed by further condensation of this reaction product with phthalyl chloride.<sup>64</sup> A typical inspection test of Santopour is given below.

TABLE 43—Properties of Santopour

|                       |       |
|-----------------------|-------|
| Gravity, ° A.P.I.     | 26.7  |
| Flash, ° F.           | 485   |
| Pour, ° F.            | +10   |
| S.U.V. at 210° F.     | 156.4 |
| Carbon residue        | 1.4   |
| Neutralization number | 0.02  |

It may be noted that, similar to Paraflow, Santopour has also a high pour test which does not affect, however, its pour point depressant qualities.

The general behavior of Santopour in mineral oil blends is similar to that of Paraflow, and need not be described in detail. The following experimental data are presented, however, for illustrating the changes in oil properties after addition of Santopour.

TABLE 44—Effect on Oil Properties of Addition of Santopour

| Properties             | Grade of Motor Oil |                  |           |                  |
|------------------------|--------------------|------------------|-----------|------------------|
|                        | S.A.E. 20          |                  | S.A.E. 30 |                  |
|                        | As is              | +0.16% Santopour | As is     | +0.16% Santopour |
| Gravity, ° A.P.I.      | 26.8               | 26.8             | 25.8      | 25.8             |
| S.U.V. at 100° F.      | 325                | 325              | 570       | 570              |
| S.U.V. at 210° F.      | 53.3               | 53.3             | 65.2      | 65.2             |
| Viscosity index        | 94                 | 94               | 89        | 89               |
| Pour point, ° F.       | +20                | -30              | +20       | -15              |
| Color, A.S.T.M.        | 6                  | 6                | 7         | 7                |
| Carbon residue         | 0.4                | 0.4              | 0.8       | 0.8              |
| Sligh oxidation number | 9                  | 9                | 8         | 8                |

The effectiveness of the commercial pour point depressants in lowering the pour point of an oil may be visualized from the following experimental data, obtained in adding various quantities of the pour point depressants to a Mid-Continent oil of S.A.E. 30 specifications, and a +20° F. pour point. The quantities of pour point depressants added to this oil are calculated on the basis of the actual quantities of active ingredients in commercial products.

Commercial products contain certain quantities of oil, which may amount to 60-80% of the total.

TABLE 45—Effect of Pour Point Depressants on Mid-Continent Oil

| Pour Point<br>of the Mixture, ° F. | Quantity of Pour Point Depressant Added<br>Depressant A | Depressant B |
|------------------------------------|---|--------------|
| 20                                 | 0.000%  | 0.000%       |
| 10                                 | 0.020%  | 0.009%       |
| 0                                  | 0.046%  | 0.020%       |
| -10                                | 0.090%  | 0.040%       |
| -15                                | 0.124%  | 0.056%       |

The following data refer to a Pennsylvania oil of S.A.E. 20 specifications, and a +20° F. pour point.

TABLE 46—Effect of Pour Point Depressants on Pennsylvania Oil

| Pour Point<br>of the Mixture, ° F. | Quantity of Pour Point Depressant Added |              |
|------------------------------------|---|--------------|
|                                    | Depressant A                            | Depressant B |
| 20                                 | 0.000%                                  | 0.000%       |
| 10                                 | 0.012%                                  | 0.005%       |
| 0                                  | 0.036%                                  | 0.015%       |
| — 10                               | 0.078%                                  | 0.038%       |
| — 15                               | 0.114%                                  | 0.060%       |

The above data show that the relative quantities of the two inhibitors required to lower the pour point of the oils to a given level are slightly different for the two oils and that the ratios also vary somewhat with the pour point to be obtained.

It is of interest to note that with some oils the addition of pour point depressants has at first no effect on their pour point which begins to change only after the quantity of depressant added is raised above a certain minimum.

### Use of Pour Point Depressants in Dewaxing Processes

The ability of pour point depressants to modify the structure of the wax crystals is sometimes utilized in dewaxing operations in order to facilitate separation of wax from the oil. It is well known that refining of oils with chemicals frequently improves their dewaxing characteristics, a phenomenon usually ascribed to the removal of the inhibitors. Similar control is sometimes obtained, however, by adding pour point depressants to oils to be dewaxed in order to obtain the desired balance. Many patents have been issued to cover the above phase of petroleum refining operations. These include addition of both natural and artificial pour point depressants, as well as pretreatment of oils with different chemicals.

Burmah Oil Co.<sup>65</sup> pretreats the oil before dewaxing with anhydrous aluminum (or similar) chloride; Lyons<sup>66</sup> pretreats the oil with clay at elevated temperatures and then utilizes the same clay as filter aid for separating the wax after chilling the mixture to low temperatures; Osterstrom and Wagner,<sup>67</sup> Henriksen,<sup>68</sup> Johnson,<sup>69</sup> and Anderson<sup>70</sup> add small quantities of asphalt to improve separation of wax in centrifuging; Manley, McCarty, and Gross,<sup>71, 72</sup> improve filtering rates by addition of a pour point depressant from cracked pressure tar; Pevero<sup>73</sup> uses for the same purpose a condensation product of an aromatic hydrocarbon; N. V. de Bataafsche Petroleum Maatschappij<sup>74</sup> employs a pyrogenic condensation product of mineral, vegetable or animal oils or fatty acids; Montgomery<sup>75</sup> adds a small amount of heavy lubricating oil stock to light lubricating oils before dewaxing them with propane; Funsten<sup>76</sup> adds a high boiling compound obtained from coal tar to the oil to be dewaxed, while Schott<sup>77</sup> uses for the same purpose a heavy residue from petroleum distillation. Jones<sup>78</sup> adds "amorphous" wax to the oil, which contains "crystalline" wax and thereby makes possible separation of crystalline wax by centrifuging. Chase and Anderson<sup>79</sup> add to the wax distillate a "crystallization regulator" obtained from a residual oil. Hopper<sup>80</sup> adds hard asphalt of 3-5 penetration (at 25° C.), and 93° C. melting point in order to facilitate the separation of wax from the oil. Quinn<sup>81</sup> adds to the wax distillate a small quantity of a

heavy hydrocarbon distillate. Texaco Development Corp.<sup>82, 83</sup> uses various condensation products obtained by heating aromatic hydrocarbons such as benzene, naphthalene, anthracene, fluorene, phenanthrene or their derivatives, with aluminum chloride. Anderson<sup>84</sup> uses a residue from the distillation of a waxy mixture in order to prevent formation of interlacing crystals; Standard Oil Development Co.<sup>85</sup> employs for this purpose wax tailings; Anderson<sup>86</sup> recommends soaps of triethanolamine; Moser<sup>87</sup> specifies various addition agents; etc.

See also a description of the use of paraffin in commercial centrifuging.<sup>88</sup>

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## Chapter XVII

### Viscosity Index Improvers

The high viscosity index characteristics of oils intended for lubricating engines operating over a wide temperature range are of considerable importance in order to insure satisfactory lubrication under a variety of service conditions. As already pointed out in Chapter I, the viscosity index is an empirical relationship based on the viscosity-temperature susceptibility characteristics of two typical crudes, and, for this reason, has no theoretical foundation. However, other proposed methods have no distinct advantages over this empirical method of classifying natural petroleum products, while the simplicity of the viscosity index concept has favored its wide adoption by the petroleum industry.

In refining natural petroleum oils it is economically possible to improve their viscosity index up to a certain maximum as further refining has only an additional negligible effect on viscosity index characteristics. Further marked improvement can be effected, however, by adding to the oil various types of substances which are described below.

#### Nature of Viscosity Index Improvers

One of the first attempts to improve the viscosity index of lubricating oils by addition of such substances was made on a commercial scale by one of the large companies which began marketing products to which metallic soaps were added. Such solutions of colloidal nature showed very satisfactory viscosity index characteristics within the temperature limits employed in the viscosity index determinations. This improvement was due to the presence of colloidal particles which are capable of raising the viscosity of solutions, such viscosity being only relatively little affected by temperature changes until, by heating such solutions to higher temperatures, a true solution is obtained.<sup>1</sup> This attempt was unsuccessful, however, as, at temperatures prevailing in the motor, the oils containing soaps showed a sudden break in their viscosities which interfered with the proper lubrication of the engines.

The failure of the soaps to maintain the viscosity of oils at high temperatures could be attributed, apparently, to the dissociation of complex molecules existing at low temperatures to single molecules at higher temperatures. Further attempts to produce satisfactory results were, therefore, concentrated towards synthesizing the required high molecular compounds consisting of large single molecules or of polymers sufficiently stable to the temperature changes to prevent their dissocia-

tion into simpler molecules. Addition of such type of molecules to a relatively low molecular weight oil was, therefore, promising as the colloidal effect of these molecules on the viscosity index of the oil would not be accompanied by a sudden break in the viscosity of the oil at high temperatures.

The favorable effect on the viscosity index of the oil of adding to light products compounds of high molecular weight type also follows from the common knowledge that by blending very high and very low viscosity oils of the same viscosity index, the viscosity index of the blend is higher than that of the arithmetical average of the component oils. The greater the difference in the viscosities of the oils used for blending purposes, the greater is the improvement in the viscosity index above the arithmetical average.

### Effect of Blending on Viscosity Index of Oils

The improving effect on the viscosity index of blending high and low molecular weight substances is particularly noticeable in the low viscosity range products. This is explained at least partially by the peculiarities of the viscosity index scale. On this scale the spread between the 0 and 100 viscosity index oils in terms of viscosities at 100° F. is much smaller for low than for high viscosity oils. Given two ideal oils, *i.e.*, oils whose viscosities do not change with temperature (the one, a light oil of, for example, 40 seconds Saybolt Universal, the other, a heavy oil of, say, 160 seconds Saybolt Universal), it will be found that the viscosity indexes of these oils will be 269 and 158, respectively. Thus, for ordinary practical oils, there is considerably more room for improvement on the viscosity index scale for lighter as compared with heavier oils.

The above discussion, however, does not make it evident why blending of light and of heavy oils actually give a product of viscosity index greater than the weighted average of the viscosity indexes of the component oils. Thus, it is possible to obtain by such blending a product of viscosity index greater than that of either component. In general, the viscosity of a blend at any given temperature is lower than the arithmetical average of the viscosities of the components at that temperature, with the lowering of the actual viscosity below the arithmetical average being the less for the higher temperature viscosities. This can be verified by reference to the usual blending charts. These divergencies of viscosities of blends from the arithmetical average of components are in the directions, of course, that produce higher viscosity indexes than the arithmetical averages of the component oils.

### Exanol

The above principles have been applied in practice for improving the viscosity index of commercial products by the I. G. Farbenindustrie

A.-G., and the Standard Oil Co. (N. J.),<sup>2</sup> who developed a special heavy resin-like synthetic material, obtained by polymerization of unsaturated hydrocarbons, which on addition to lubricating oils raises considerably their viscosity index. The product is known by the trade name "Exanol" and can be bought separately for adding to lubricating oils which are already in the automobile crankcase and which do not contain it.<sup>3</sup> Oils containing these types of substances are likewise marketed under the trade name of "Univis." The effect on their viscosity indexes of adding "Exanol" to various lubricating oils is shown in the following table.<sup>4, 5</sup>

TABLE 47—Effect on Viscosity Index of Addition of "Exanol"

| Base                | Exanol<br>%<br>Added | Saybolt Viscosity |         | V. I. |
|---------------------|----------------------|-------------------|---------|-------|
|                     |                      | 100° F.           | 210° F. |       |
| Coastal distillate  | 0                    | 358               | 49.2    | 26    |
|                     | 0.5                  | 441               | 54.0    | 51    |
|                     | 1.5                  | 627               | 66.0    | 80    |
|                     | 3.0                  | 1,020             | 91.5    | 99    |
|                     | 5.0                  | 1,851             | 147.5   | 111   |
| 90 V. I. distillate | 0                    | 296               | 51.4    | 91    |
|                     | 0.5                  | 353               | 55.4    | 100   |
|                     | 1.0                  | 418               | 60.6    | 106   |
|                     | 2.0                  | 561               | 73.0    | 114   |
|                     | 5.0                  | 1,322             | 136.0   | 125   |
| Pennsylvania oil    | 0                    | 237               | 49.0    | 100   |
|                     | 0.5                  | 273               | 52.0    | 106   |
|                     | 1.0                  | 332               | 58.4    | 119   |
|                     | 2.0                  | 432               | 68.6    | 126   |
|                     | 5.0                  | 1,050             | 124.0   | 128   |

The effect of adding "Exanol," on various properties of the oil other than viscosity index, is shown in the following table.<sup>5</sup>

TABLE 48—Effect of Adding "Exanol" on Properties of Lubricating Oils

|  | Paraffinic<br>Base<br>Stock<br>"A" | Base<br>Stock<br>"A"<br>+ "Exanol" | Paraffinic<br>Base<br>Stock<br>"B" | Base<br>Stock<br>"B"<br>+ "Exanol" | Paraffinic<br>Base<br>Stock<br>"C" | Base<br>Stock<br>"C"<br>+ "Exanol" |
|--|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| A.P.I. gravity                         | 30.7                               | 30.7                               | 30.2                               | 29.6                               | 28.6                               | 28.5                               |
| Flash point (deg. F.)                  | 420                                | 420                                | 425                                | 425                                | 445                                | 440                                |
| Viscosity at 100° F.                   | 195                                | 343                                | 254                                | 598                                | 488                                | 882                                |
| Viscosity at 210° F.                   | 45.5                               | 60                                 | 49.2                               | 77.8                               | 64.6                               | 92                                 |
| Viscosity index                        | 98                                 | 123                                | 92                                 | 119                                | 100                                | 117                                |
| Color                                  | 22½                                | 20½                                | 17½                                | 17                                 | 1½                                 | 1½                                 |
| Conradson carbon<br>residue (per cent) | 0.008                              | 0.014                              | 0.018                              | 0.021                              | 0.722                              | 0.794                              |
| Pour point (deg. F.)                   | 10                                 | 10                                 | 10                                 | 10                                 | 30                                 | 30                                 |

### Univis Oils

The properties of the commercial Univis oils are claimed to be those listed in the following table.<sup>6</sup>

TABLE 49—Properties of Commercial Univis Oils

| Saybolt Universal<br>Viscosity at ° F. | Univis | Naphthenic<br>Base Oil | Univis | Univis | Paraffinic<br>Base Oil | Univis |
|--|--------|------------------------|--------|--------|------------------------|--------|
| 210                                    | 40.7   | 39.4                   | 47.9   | 62.4   | 56.8                   | 77.4   |
| 130                                    | 64.5   | 68                     | 93     | 153    | 175                    | 217    |
| 100                                    | 95     | 113                    | 150    | 264    | 368                    | 388    |
| 70                                     | 167    | 242                    | 282    | 520    | 980                    | 775    |
| 30                                     | 500    | 1,100                  | 880    | 1,670  | 5,700                  | 2,630  |
| 0                                      | 1,500  | 5,500                  | 2,750  | 5,300  | 33,000                 | 8,800  |
| — 20                                   | 3,900  | 22,000                 | 7,000  | 14,000 | 165,000                | 22,000 |
| Viscosity index                        | ....   | ....                   | 153    | 150    | 101                    | 146    |

Addition of the above type of substances is claimed to yield oils which are stable, do not produce ring sticking, and have no stringiness, all three of which characteristics are observed when improvement in viscosity index is obtained by adding to the mineral oils various types of fatty oils or rubber. According to Calkins,<sup>7</sup> however, stability of the above type of materials as typified by "Uniflow," "Exanol," "Paraton," etc., has not been proven by the early service experiences. It should also be noted that introduction of very light oils in such blends may cause their rapid evaporation in engines with insufficient provisions for cooling. The partial removal of these components from the blends will, therefore, be associated with a corresponding increase in the viscosity of the oil and lowering of the viscosity index thus nullifying to a certain extent the advantages gained by employing products of an initial high viscosity index, if these products are improperly balanced.

### Proposed Viscosity Index Improvers

A great number of patents have recently been issued for adding various materials to petroleum oils with the purpose of improving their viscosity index characteristics, as a variety of high molecular weight compounds may be employed for this purpose.

Wulff and Breuers,<sup>8</sup> and I. G. Farbenindustrie A.-G.,<sup>9</sup> specify for this purpose polymerized vinyl ester of stearic acid and similar oxygenated vinyl compounds; Davis<sup>10</sup> uses polymerization products produced from materials consisting mainly of straight hydrocarbon chains of at least ten hydrocarbon atoms of the type of waxy hydrocarbons and their oxygenated derivatives, such as alcohols, aldehydes, ketones and esters; Pier, Christmann, and Donath,<sup>11</sup> and I. G. Farbenindustrie A.-G.,<sup>12</sup> use substances of a mean molecular weight not less than 500 and obtained by destructive hydrogenation of polymerization products of unsaturated hydrocarbons, *e.g.*, rubber, polymerization products of diolefins, or natural or synthetic resins; I. G. Farbenindustrie A.-G.<sup>13</sup> uses substances having a molecular weight of above 600 which are obtained by condensing or polymerizing hydrocarbons, such as condensation products of paraffin wax and naphthalene; Mikeska and Fulton<sup>14</sup> specify polystyrene resins; Pier,<sup>15</sup> and I. G. Farbenindustrie A.-G.,<sup>16</sup> refines lubricating oils with propane for removing asphalt and wax and adds to the oil a synthetic high molecular weight product richer in hydrogen than the precipitated asphalt; Eichwald<sup>17</sup> empolys polymerized fatty oils; Pevere<sup>18</sup> recommends semi-liquid products present in oxidized paraffin wax and consisting of only a minor proportion of acids and a major proportion of other saponifiable compounds, including esters, such products containing substantially no unoxidized wax; N. V. de Bataafsche Petroleum Maatschappij<sup>19</sup> uses esters, ethers, mixed esters, or mixed

ester-ethers of cellulose or similar highly polymerized hydrocarbons, such as tri-stearyl cellulose; Ruhrchemie A.-G.<sup>20</sup> specifies polymerization products obtained by treating gases containing ethylene and propylene with condensing agents such as aluminum chloride, iron chloride, zinc chloride or boron fluoride; Standard Oil Development Co.<sup>21, 22</sup> adds to the oil an oil soluble linear polymer of *iso*-butylene which has a molecular weight higher than 30,000; Standard Oil Development Co.<sup>23</sup> and Fulton and Mikeska,<sup>24</sup> recommend condensation product of ethylene dichloride and benzene or similar polymers of the nonasphaltic chain type comprising alternate aromatic rings and aliphatic chains; I. G. Farbenindustrie A.-G.<sup>25</sup> adds to the oil up to 10% of condensation products obtained by subjecting hard or white paraffin to the action of a silent electric discharge; Standard Oil Development Co.<sup>26</sup> employs high molecular weight, oil soluble, oxygen free polymerization products of acetylene or acetylene derivatives; etc.

In chapters on deasphalting it has already been shown that removal of asphalt from oils frequently results in a lowering of their viscosity index which is due to the elimination of high molecular weight colloidal type of substances in the course of deasphalting operations. However, the use of asphalt for improving the viscosity index of oils is, obviously, impractical due to the instability of the resulting mixtures.

By comparing the nature of viscosity index improvers and pour point depressants it may be noted that, although of apparently different chemical structure, they are in many respects similar by being high molecular weight substances. For this reason, viscosity index improvers often, but not necessarily always, possess the pour point depressant qualities, while the pour point depressants are also capable of improving the viscosity index. The differences between the two types of these additives is frequently more in the relative degree of improvement in these two oil characteristics than in the actual differentiation between the two inherent properties of these substances. For this reason, oils prepared by using viscosity index improvers need be only partially dewaxed, as the quantity of the resinous materials added for improving the viscosity index of an oil is usually more than sufficient for lowering the pour point to the required specifications.

### Pre-Diluted Oils

As already briefly mentioned, viscosity index improvement is likewise obtained by diluting the oil with light petroleum fractions, such as kerosene or heavy naphtha. In cold weather the heavy gasoline fractions tend to concentrate in the crankcase due to excessive choking and the necessity of using relatively rich gasoline-air mixtures. With engines having no special provision for eliminating these dilution effects, the oil finally becomes diluted with such light fractions until equilibrium conditions are reached. The oil diluted in this way offers, however, less friction in starting than the same oil before dilution occurred. In order to avoid such difficulties with fresh oils it has been recommended to pre-dilute them with light petroleum distillates to the extent corresponding to the equilibrium conditions reached in the engine. Such oils<sup>27</sup> are being used commercially, although their utility becomes of increasingly less

importance with the latest improvements in engine design. Diluted oils of the above type have a higher viscosity index than the basic oil used in the blend. Such improvement in the viscosity index can be also obtained by employing other diluents than naphtha, such as carbon tetrachloride,<sup>28</sup> etc., which may possess in addition to the properties of improving the viscosity index also some oiliness characteristics, etc., as discussed in the next chapter. The use of these diluents in lubricating oils is limited, however, due to their volatility.

It has been mentioned also that the presence of wax in petroleum oils tends to improve their viscosity index. Patents, therefore, have been issued which specify improvement in viscosity index by introducing into the oils a certain amount of wax with a pour point depressant to offset the resulting rise in the pour point.<sup>29</sup> Up to the present time, however, such methods have not been applied in practice, as the viscosity index improvement which may be obtained in this manner is considerably less than that obtainable with the synthetic compounds.

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## Chapter XVIII

### Oiliness Carriers

One of the major requirements of a good lubricant is its ability to maintain a film between the moving metal surfaces and, thus, eliminate direct metal to metal contacts. This problem is not of particular importance when the clearances between the moving parts are large. Under the latter operating conditions the viscosity of the oil is of primary importance and determines the satisfactory behavior of this oil in the engine.

#### Oiliness

However, with increased bearing pressures the oil tends to be gradually squeezed out of the bearings with the resulting increase in the friction coefficient. At still higher pressures the oil is completely displaced from the bearings and metal to metal contacts are established. The tenacity with which a given oil is capable of adhering to the metal at such high bearing pressures is commonly referred to as "oiliness." Oiliness is usually defined as that property of the oil which can make a difference in the friction when two lubricants, having the same viscosity at the temperature of the film and at atmospheric pressure, are used under identical conditions.<sup>1</sup> Experimental work has shown that oiliness of lubricants may be improved by addition of the various types of substances which are discussed below.

When the pressure between the moving parts is increased, however, to a point when none of the known lubricants is capable of maintaining the film between the metal surfaces, direct metal to metal contacts become inevitable. Such conditions are encountered, for instance, in lubrication of automobile gears where pressures between the gear teeth may reach values as high as 400,000 lbs. per square inch with rubbing velocities ranging from zero to 300 feet per minute.<sup>2</sup> Under such conditions the main function of the lubricant is to prevent seizure between the moving parts by properly preparing their surfaces so as to insure minimum friction and lowest possible rate of deterioration when the surfaces are brought into intimate contact while the engine is operating.

Omitting the discussion of the, as yet, rather insufficiently clarified mechanism of the action of lubricants under high pressures, it is feasible to assume, however, that at low bearing pressures the oil is capable of protecting the bearings irrespective of the tenacity with which it adheres to the metal. At increased pressures the ability of the oil to adhere to the

metal becomes of increasingly greater importance, while, at very high pressures, chemical action of the lubricant on the rubbing surfaces is required in order to insure the presence of smooth surfaces even after they are slightly injured by direct metal to metal contacts. In the discussion below, only the oiliness or lubricity carriers, or substances assisting in establishing oil films at moderate bearing pressures, are being considered. Problems connected with the extreme pressure lubricants which are satisfactory for very high bearing pressures involve the use of different type of lubricants. Such lubricants, due to their chemical composition, may be regarded, to a certain extent, as mixtures of chemicals where the oil functions primarily as a blending medium and not as a lubricant in the strict sense of this word. Within certain limitations, however, the oiliness carriers and the extreme pressure lubricants resemble each other in being substances of more or less slightly corrosive nature. This is not unexpected, however, as a substance capable of maintaining a tenacious film around the metal surface must possess a certain degree of affinity towards the metal, while the high pressure lubricants should be moderately corrosive so as to insure an actual chemical effect on the metal surfaces in order to maintain their smoothness.

Many methods have been proposed for measuring the relative degree of oiliness possessed by various lubricants, but no standardization along these lines has yet been accomplished.

Woolgar<sup>3</sup> describes various devices proposed for measuring oiliness characteristics of lubricants. Breth and Liberthson<sup>4</sup> recommend the use of a rather novel method of measuring oiliness by employing centrifugal force, using the Sperry-Cammen Adheroscope.

The difficulty is further increased by the difference in the results obtained with various testing devices which frequently disagree in evaluating oiliness characteristics of lubricants. No satisfactory and generally adopted system of measuring oiliness in numerical units has yet been accepted, although some attempts are now being recorded in reporting oiliness in terms of an "oiliness index,"<sup>4</sup> instead of the more or less arbitrary units. As a result, in the opinion of some workers in this field, no conclusive evidence has been produced yet on the beneficial effects of the addition of oiliness carriers to lubricating oils,<sup>5</sup> while others consider that usefulness of such carriers has been definitely proven.<sup>6, 7</sup>

### **Oiliness of Mineral Oils**

The straight mineral oils may be generally considered as possessing approximately the same degree of oiliness irrespective of the nature of the crude or of the treating methods employed in their manufacturing. The observed differences between the oils are, as a rule, insufficient to be considered of practical importance. In this respect, mineral oils are inferior to vegetable or animal oils, addition of which to mineral oils is, therefore, recommended. Nevertheless the degree of oiliness associated with the

mineral oils is usually more than sufficient for all practical purposes, including motor lubrication, as in well lubricated bearings the loads rarely exceed 2,000 lbs. per square inch and the rubbing speeds are usually high enough to maintain a constant film of oil for separating the bearing and the journal. When loads are high, however, such as in engines during the break-in period or in special types of industrial machinery, it is frequently desirable to improve the oiliness of lubricating oils by the addition of special oiliness carriers.

### Oiliness Carriers

Of the substances used for improving oiliness of lubricating oils, oleic acid was until recently of some commercial importance,<sup>8</sup> being used in manufacturing the so-called "germ-processed" oils. Addition of this acid to the oil in quantities as low as 0.5% is usually sufficient to insure the desired degree of improvement in oil properties. Stearic acid is claimed to be even more effective in this respect than oleic acid but it is not as suitable for practical purposes due to its low solubility characteristics. The use of stearic acid as well as other acids containing at least sixteen carbon atoms in the molecule, such as arachidic or cerotic acids, is nevertheless recommended in some of the patents.<sup>9</sup>

Mildly oxidized vegetable oils,<sup>10</sup> as well as various derivatives of organic acids, particularly esters, are also recommended.<sup>11</sup>

Other groups of substances used for improving oiliness characteristics include halogenated organic derivatives, of which chlorinated esters of stearic acid appear to be particularly promising and are being used commercially.

Lincoln and Henriksen<sup>12</sup> use halogenated organic esters; Lincoln and Henriksen,<sup>13</sup> and Henriksen and Hartzell,<sup>14</sup> recommend chlorinated stearic acid or similar compounds; Henriksen and Lincoln<sup>15</sup> employ halogenated amides of aliphatic acids, such as chlorinated *o*-tolyl stearamide or sulfochlorinated *o*-tolyl stearamide; Continental Oil Co.<sup>16</sup> specifies halogenated organic oxygen compounds including ethers, alcohols, aldehydes, ketones, acids or esters; Henriksen and Lincoln<sup>17</sup> use a condensation product of chlorinated stearic acid and diphenylene oxide or similar derivatives; Lincoln and Henriksen<sup>18</sup> specify condensation products such as derived from chlorinated lard oil and naphthalene; Lincoln and Henriksen<sup>19</sup> cover condensation products derived from two halogenated fatty acids or halogenated esters; Lincoln and Henriksen<sup>20</sup> use halogenated wax and halogenated organic acid condensation product, such as derived from chlorinated paraffin and chlorinated stearic acid; Henriksen and Lincoln<sup>21</sup> use a halogenated diphenylene oxide; Henriksen and Lincoln<sup>22, 23</sup> recommend halogenated aromatic hydrocarbons of the phenylbenzene group. Davis, Sibley, and Lincoln,<sup>7, 24</sup> and Lincoln and Byrkit,<sup>25</sup> discuss the effects of chlorinated aliphatic acid esters on the oiliness characteristics of oil to which they are added, while Clark, Sterrett, and Lincoln<sup>26</sup> present the results of their studies on similar substances by the X-ray diffraction methods; Lincoln and Henriksen<sup>27</sup> recommend condensation products which contain a small amount of halogens in organic combination; Moran<sup>28</sup> patented the use of Nicolet and de Mitt's acid; Steiner<sup>29</sup> specifies halogenated terpenes; Prutton and Smith<sup>30, 31, 32, 33, 34</sup> enumerate a large number of halogenated organic derivatives suitable for improving oiliness of lubricants.

Nitriles,<sup>35</sup> nitroaromatics and amines,<sup>36</sup> and various sulfur compounds,<sup>37</sup> are also included in different patents.

Ralston, Christensen, Hoffman, Selby, and Conquest,<sup>38</sup> discuss the use of fatty acids, nitriles, amides, ketones, thioamides and other substances with the particular reference to extreme pressure lubricants. Byers<sup>39</sup> gives a survey of patent literature on extreme pressure lubricants.

It is likewise claimed that the acids present in petroleum oils before refining possess the desired oiliness characteristics,<sup>40</sup> and that similar desirable substances may be obtained by oxidizing various petroleum products,<sup>41</sup> or aliphatic hydrocarbons of mineral origin.<sup>42</sup>

### Effect of Oiliness Carriers on Oil Properties

In employing the various oiliness carriers in practice care should be exercised, however, that a real and not a seeming degree of improvement is obtained in the oiliness properties of the lubricant and that other properties of this lubricant, particularly, its oxidation stability are not unfavorably affected.

It should be noted that some of the oiliness carriers may improve the pour point of the oil,\* and exert not only a beneficial, but also a deleterious effect on some of the other oil properties. In choosing an oiliness carrier for practical use, therefore, considerable attention must be given to evaluating its various effects on the finished oil.

Due to the oiliness characteristics of organic acids opinions have been expressed that oils oxidized in service may be more desirable for lubricating the engine than fresh oils which do not contain such oxidation products. However, such observations refer only to improvements in one specific characteristic of the oil and do not take into account deterioration in other oil properties.

As already mentioned substances of similar nature to that of the oiliness carriers are used for extreme pressure lubricants and frequently the difference between the two types of lubricants is only in the amount and not in the chemical composition of the compounds added to the oil. Cutting oils as well as other specialized products require addition of similar substances for insuring their best performance, but they are omitted from the present discussion due to their highly specialized nature.

\* Ralston and Christensen<sup>43</sup> employ mixed ketones for improving both oiliness and pour point of oils; Christensen and Selby<sup>44</sup> employ for the same purpose condensation products of higher fatty chlorides and the coal tar products.

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## Chapter XIX

### Oxidation Inhibitors

One of the most important characteristics of lubricating oils is their stability in service. A motor oil is frequently required to last for at least 2,000 miles or more of driving while some drivers even consider that changing of the oil is superfluous, particularly, if their cars are equipped with filters. Transformer and turbine oils remain in service for a number of years, while the life of cable oils is estimated as being 20 years or even longer. These drastic operating conditions require an unusual stability from oils released to the market and consequently a careful attention to the refining methods employed in their production.

#### Oxidation Inhibitors

As already mentioned the original conception of oil stability has been associated with the inherent resistance of the oil molecules towards oxidation, and oil refining was supposed to eliminate from the finished oil all of the unstable molecules present. This conception prevailed until the classical work of Moureu and Dufraisse<sup>1</sup> revealed the existence of oxidation inhibitors, or substances which are capable of protecting less stable molecules from oxidation even when such substances are present in exceptionally small quantities,—a few tenths or even a few thousands of one per cent on the volume of the oil. A description of inhibitors has been given by Kalichevsky and Stagner,<sup>2</sup> and need not be repeated in detail, except for the following generalizations:

1. The presence of minute quantities of certain substances in an oil may either promote or retard the oxidation of the oil when exposed to the action of air or free oxygen.
2. The same substance may act as a promoter or as a retarder of the oxidation reactions depending on the concentration of this substance, nature of substances present in the oil, and the conditions of oxidation.

From the above, it follows that in investigating the oxidation inhibitors it is important to determine the optimum quantity of the inhibitor required for protecting the oil from oxidation and not to restrict its amount to a certain arbitrary concentration, to carry out the experimental work under conditions approaching as closely as possible those encountered in service, and to employ the inhibitors in the particular oil which they are intended to protect.

Inhibitors were first applied successfully in the petroleum industry for protecting light petroleum distillates such as gasolines, but, gradually, their use has been extended to cover a variety of heavier petroleum products. In carrying out such investigations it was soon discovered that the degree of refining to which the oils were subjected has a great influence on the inhibitor response. The highly refined oils, which are obviously more uniform in their composition than lightly refined oils, are, in general, easier to protect from oxidation by means of inhibitors than oils which are less drastically refined. Such behavior of lightly refined oils may be, probably, ascribed to the different oxidation reactions to which the various oil constituents are susceptible, and to the fact that, for protection of oils containing widely different classes of hydrocarbons, more than one inhibitor may be required to protect them from oxidation. However, inhibitors are known which are capable of protecting some of the rather lightly refined oils for relatively long periods of time.

### **Types of Oxidation Inhibitors**

Inhibitors which were first proposed for protecting the lubricating oil fractions from oxidation could be classified into three distinct groups: hydroxy compounds, such as phenolic derivatives, naphthols, etc., nitrogen compounds, like naphthylamines, aniline derivatives, etc., and sulfur compounds, as represented by elementary sulfur, disulfides, etc. The list was soon extended to cover compounds of organo-metallic type and of chlorine, while the extension of the search towards the elements belonging to similar groups in the periodic system revealed the anti-oxidant properties of derivatives of phosphorus, arsenic, antimony, selenium and tellurium.

Byers<sup>3</sup> gives a complete list of patents (a total of 69), and their brief description covering the names and the uses of various chemicals, recommended as oxidation inhibitors for lubricating oils.

### **Effect of Metals in Oxidation Tests**

Until recently, however, the use of inhibitors in the lubricating oil fractions has been confined primarily to transformer and turbine oils which were discussed in the aforementioned book by Kalichevsky and Stagner. In such investigations relatively little attention was paid to the effect of the metals with which the oils are brought in contact when in service, although in the newly developed oxidation tests usually attempts are being made to introduce the necessary corrections by employing the same types of metals with which the oils are brought in contact in commercial installations. Comparison of the results of oxidation tests performed in the presence and absence of metals often show considerable discrepancies, as oils stable in absence of metals may deteriorate relatively fast in their presence and vice versa. Thus the well known "Life" test for transformer oils is now being practically discarded by the industry

as an indicative test of the stability of oils in service and other tests employing metals are now being frequently employed in its place. It should also be noted, however, that the temperature at which the oxidation test is made is of very considerable importance. This temperature should be maintained as closely as possible to that encountered in practice as otherwise the results may be misleading. Unfortunately, however, accelerated tests cannot be entirely discarded because the time element involved in normal temperature tests may become prohibitive for investigational purposes.

The presence of metals in oxidation tests introduces additional complications in the hypothetical explanation of the mechanism of the action of anti-oxidants. It has been known for many years that the surface of the metal has a great effect on its catalytic activity, and that entirely different results may be obtained, if the surface is freshly polished, or if no attempts are made for its renovation. It has been noted also that oils which are relatively poorly refined may show exceptional stability when subjected to oxidizing conditions in presence of metals in comparison with better refined oils which show greater stability than the poorly refined oils in absence of metals.

The above observations may be explained by the action of the oil on the surface of the metal. A sludge forming oil coming in contact with the metal tends to deposit sludge on the metal surface, this sludge film protecting the remaining body of the oil from further action of the metal.<sup>4</sup> A highly refined oil is incapable, however, of forming such a protective film and remains in contact with the metal during the entire time of the test. The test is thus made more severe for highly refined oils than for less drastically refined ones.

### Corrosion Inhibitors

The above conception leads to a further assumption that inhibitors added to the oil oxidized in presence of metals may act not only as true anti-oxidants but also as substances passivating the catalytic activity of metals. Such types of anti-oxidants will form a coating on the surface of the metal, this coating being formed either by deposition of a dense film of sludge or by formation of thin layers of metallic compounds produced by direct action of the inhibitors on the metal.

Among the new types of inhibitors which recently have achieved commercial importance, compounds of phosphorus are of considerable interest as their protective action seems to be best explained by the above surface theory. Besides phosphorus and related elements, such as arsenic or antimony, organic compounds of chromium, bismuth, mercury, and other metals appear to have a similar action. Thus it is claimed that a good lubricant should contain organic chromium compounds for preventing catalytic action of iron in the engine, and organic tin compound for preventing deposition of carbon, and an organic lead compound for

preventing ignition or cracking. Chromium and tin oleates, and lead tetraethyl are given as examples of such compounds.

N. V. de Bataafsche Petroleum Maatschappij<sup>5, 6</sup> employs organic compounds of phosphorus and arsenic, such as phosphoric acid esters; van Dijk<sup>7</sup> adds compounds of phosphorus, arsenic, selenium or tellurium; E. I. du Pont de Nemours and Co.,<sup>8</sup> specifies phosphoric acid esters; Prutton and Smith<sup>9</sup> recommend esters of thiophosphoric acid and, particularly, their halogen derivatives; Byers<sup>10</sup> lists patents covering phosphorus, chlorine and sulfur compounds which are useful in extreme pressure lubricants, and Byers<sup>9</sup> gives a similar summary of patents on sulfur, nitrogen and hydroxy compounds acting as anti-oxidants.

Wakefield and Co., Ltd.,<sup>11</sup> Towne,<sup>12</sup> Evans,<sup>13</sup> Rosen,<sup>14</sup> Standard Oil Development Co.<sup>15</sup> add to the lubricant an organo-metallic compound containing two metal atoms in the molecule, such as  $(\text{CH}_3)_2\text{Sn} \cdot \text{Sn}(\text{C}_6\text{H}_5)_2$  or other similar compounds of lead, bismuth, mercury, thallium and arsenic. Desmarais frères<sup>16</sup> employ aluminum stearate, oleate or naphthenate. Griffith and Helmore<sup>17</sup> recommend chromium compounds, while Ducamp<sup>18</sup> specifies mercury compounds; Gilbert<sup>19</sup> uses nickel compounds; Gilbert<sup>20</sup> covers compounds of cobalt; Sullivan, Shoemaker, and Taylor<sup>21</sup> disperse in the oil sodium carbonate; see also Mardles<sup>22</sup> on the use of tin compounds.

As an illustration of the improving effect of corrosion inhibitors on the properties of lubricating oils, the following experimental data are presented which refer to an organic phosphite known commercially as "Santolube C.C."<sup>23</sup> In these tests, oil at 350° F. was played upon the bearing in a jet, by means of a circulating pump, which maintained a pressure of 35 lbs. per sq. inch in the discharge line. Air was then bled through a Number 75 drill hole into the oil stream immediately ahead of the pump action. Losses in weight of the bearings at the end of periods of 20-24 hours were determined.

TABLE 50—Effect of Adding "Santolube C.C." to Lubricating Oil

*A. Tests on Copper-Lead Bearings*

|  |                |
|--|----------------|
| Grade of oil                                       | S.A.E. 20      |
| Temperature of oil                                 | 350° F.        |
| Time of test                                       | 24 hours       |
| Weight loss in oil without inhibitor               | 117 milligrams |
| Weight gain in oil containing 0.25% Santolube C.C. | 7 milligrams   |

*B. Tests on Cadmium-Silver Bearings*

|  |                 |
|--|-----------------|
| Grade of oil                                       | S.A.E. 20       |
| Temperature of oil                                 | 350° F.         |
| Time of test                                       | 20 hours        |
| Weight loss in oil without inhibitor               | 1070 milligrams |
| Weight loss in oil containing 0.25% Santolube C.C. | 6 milligrams    |

In a different jetometer, using S.A.E. 20 oil at a temperature of 350° F., the following weight losses resulted during the 20 hour test period:

|  |                 |
|--|-----------------|
| Weight loss in oil without inhibitor               | 1450 milligrams |
| Weight loss in oil containing 0.25% Santolube C.C. | 16 milligrams   |

The effectiveness of corrosion inhibitors is also demonstrated by the following tests, using a single cylinder Delco engine equipped with cadmium-silver bearings. S.A.E. 20 grade oil containing 0.25% Santolube C.C. is compared with the same grade oil containing no inhibitor. During the runs the oil temperatures were held at 330° F. At the end of 20 hours and, again, at the end of 40 hours, losses in weight and in thickness of the bearings were determined.

TABLE 51—Effect of Adding Corrosion Inhibitor to S.A.E. 20 Grade Oil

|  | As is          | S.A.E. 20 Oil<br>+ 0.25% Santolube C.C. |
|--|----------------|---|
| Weight loss after 20 hours, milligrams   | 5052           | 122                                     |
| Loss in thickness after 20 hours, inches | 0.004          | 0.0001                                  |
| Weight loss after 40 hours, milligrams   | not determined | 6706                                    |
| Loss in thickness after 40 hours, inches | not determined | 0.004                                   |

Addition of such small quantities of corrosion inhibitors has usually only a small effect on general characteristics of lubricating oils, which may be disregarded. This is exemplified by the data given in the following table.

TABLE 52—Effect of "Santolube C.C." on Characteristics of Lubricating Oils

|                       | As is | S.A.E. 20 Oil<br>+ 0.50% Santolube C.C. |
|-----------------------|-------|---|
| Gravity, ° A.P.I.     | 30.6  | 30.5                                    |
| S.U.V. at 100° F.     | 310   | 303                                     |
| S.U.V. at 210° F.     | 55.8  | 55.6                                    |
| Viscosity index       | 116   | 116                                     |
| Flash point, ° F.     | 425   | 420                                     |
| Fire point, ° F.      | 480   | 475                                     |
| Pour point, ° F.      | 10    | 10                                      |
| Neutralization number | 0.0   | 0.3                                     |
| Color, A.S.T.M.       | 6     | 6                                       |
| Carbon residue        | 0.3   | 0.3                                     |

In employing inhibitors for passivating the surface of the metal particular care should be exercised, however, in their proper selection. If such an inhibitor actually attacks the metal surface the coating on the surface of the metal thus produced should act as protection not only for the oil, but also for preventing further attack on the metal by the inhibitor. Otherwise the metal may gradually deteriorate and lose its mechanical strength until failure occurs. Such films should not be brittle, as under service conditions they may be continually removed from the metal surface exposing fresh surfaces of metal to the attack of the inhibitor.

The above discussion had as its purpose an exposition of new theories of action of oxidation and of the so-called corrosion inhibitors. These theories may undergo changes with further progress of our knowledge of the inhibitor action. They tend to show, however, that the former theories of anti-oxidants are not sufficient to explain the mechanism

of action of all the inhibitors developed. As a result the field is still open to new discoveries and empirical methods of locating new inhibitors cannot be yet entirely abandoned in favor of purely theoretical deductions.

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## Chapter XX

### Fluorescence Improvers

As is well known, extensive refining of lubricating oils with sulfuric acid or solvents results in a considerable loss of their fluorescent characteristics. This is, generally, undesirable except in manufacturing highly specialized colorless oils, such as medicinal oils, because the majority of customers still continue to believe that the green fluorescence of Pennsylvania oils is an indication of their high quality.

#### Importance of Oil Fluorescence

However, fluorescence of oils has some desirable aspects from the sales viewpoint. Highly fluorescent oils are usually inspected in reflected and not in transmitted light. The condition of the main body of the oil, therefore, escapes inspection. In service, oils tend to develop black carbonaceous material which remains at least partially suspended in the oil. If the oil is fluorescent and is examined in reflected light, the presence of these black particles is concealed and the oil continues to appear relatively little altered. When the non-fluorescent oils are examined in transmitted light all these black particles are distinctly visible, and the black appearance of the oil leaves the customer with the impression that the oil has deteriorated rapidly in service. Actually, however, the fluorescent oil may contain considerably larger quantities of carbonaceous materials and may have deteriorated to a much larger extent than the non-fluorescent oil rejected by such visual inspection.

The exact nature of the fluorescent substances present in lubricating oils is not yet well known, but there are strong indications that their presence is rather undesirable because they appear to have an unfavorable effect on the carbon residue and on the carbonization characteristics of oils in service. This does not preclude the possibility that the quantity of at least some of such fluorescent bodies required to impart the desired fluorescence to an oil may be sufficiently small so as not to affect to any great extent the desirable characteristics of the oil and make it unfit to service. It is certain, however, that neither fluorescence nor the color of the oil are indicative of the oil quality, irrespective of whether the oil is fresh or used.

#### Ideal Dyes

The above considerations induced some of the refiners to develop various dyes which are added to lubricating oils in order to impart to

them the fluorescence characteristics of the oils from Pennsylvania crudes. The general requirements from such dyes, besides the ability of properly coloring the oils, are as follows:

(1) The dye should have no detrimental effect on any of the oil properties which determine satisfactory performance of the oil in service.

(2) The dye must be stable under usual service conditions as, due to reasons already explained, it is also intended to conceal the actual appearance of the oil when in service.

(3) The presence of the dye in the oil should not be detected by the customer by an unnatural appearance of such oils because the customer is not yet accustomed to the use of colored lubricating oils although he has become familiar with dyed gasoline.

(4) The dye should be difficult to remove from the oil by simple chemical methods, as, due to the present state of market requirements, it may serve as a pretext for the competitor to expose the presence of dye in an oil to the customer and thus to unfavorably influence his opinion.

(5) The dye should be reasonably cheap, although this requirement is usually secondary due to the exceptionally small quantities of dye employed for coloring the oil. These quantities are frequently not over 10-20 milligrams of dye per gallon of oil and may be considered as being negligible.

It seems questionable, however, whether a dye answering all of the above requirements has been yet developed, and the refiner is always required to give the individual dyes, which are now available on the market, a careful scrutiny before adopting them for commercial use.

### Fluorescence Addition Agents

Substances recommended for imparting fluorescence to lubricating oils are frequently derived from petroleum, but a number of synthetic organic dyes have also been developed for this purpose. The dyes obtained from petroleum are, however, usually considerably less efficient in imparting fluorescent properties than the synthetic ones.

One of the first dyes proposed for petroleum oils was the so-called dimethyl-crackene developed by the Royal Dutch-Shell Co. and obtained by the action of aluminum chloride on naphthalene.<sup>1</sup> Other dyes obtained from the various petroleum or related products include cracked residua refined with sulfuric acid and clay,<sup>2</sup> or dyes obtained therefrom,<sup>3</sup> oil coloring portion of the pitch from pyrolytic decomposition of a hydrocarbon oil,<sup>4</sup> coloring substances obtained by interaction of aluminum chloride with petroleum oils,<sup>5</sup> aluminum chloride condensation products of liquid sulfur dioxide extracts and anthracene,<sup>6</sup> polymers of the asphaltene-like type which are obtained from spent clay through which the oil was filtered,<sup>7</sup> liquid products obtained by polymer-

ization of the liquid sulfur dioxide extracts,<sup>8</sup> hydrocarbon oils containing green fluorescent substances extracted from a coal tar residuum,<sup>9, 11</sup> condensation products of liquid monoolefins with 20-70% of polynuclear organic substances obtained in the presence of aluminum chloride,<sup>10</sup> etc. It is also recommended for imparting fluorescence to the oils to contact such oils with clay in presence of a coal-tar distillate,<sup>11</sup> or with finely divided cracking still coke.<sup>12</sup> Synthetic dyes include aminophenylbenzylthiazole or other primuline bases,<sup>13</sup> organic dyes of a heterocyclic structure containing oxygen in the structure, such as 6,12-dimethylcoeroxene, 6,12-dimethylcoeroxenol or one of its acetates, triphenyldioxazine; triphenylbenzofuran or substitution products thereof,<sup>14</sup> dyes obtained by heating a mixture of a water-insoluble soap, stearic acid, and a dye of the acridine, rhodamine, cosine or eurhodin type,<sup>15</sup> various aniline dyes,<sup>16</sup> products obtained by heating naphthenic acids with acridine orange bases,<sup>17</sup> compounds of the ceranthrene or cerbiantrenic series, such as ceroxene (yellow with green fluorescence), 1,5-diceramidonine (crimson with yellow-red fluorescence), 10-methylbenzoceroxene (red yellow with greenish fluorescence), 14-methylcerthienol-10 acetate (yellowish with green fluorescence) or acetyl compounds of ceramindenol (red with yellow-red fluorescence)<sup>18</sup> hydrocarbons obtained by heating pyrene in presence of aluminum chloride,<sup>19</sup> polymers produced from normally gaseous hydrocarbons,<sup>20</sup> compounds obtained by heating anthraquinone, benzanthrone or similar substances or their derivatives,<sup>21</sup> and others. Addition to the oil of 0.01-0.3% of furfural before subjecting the oil to a sulfuric acid treat may also improve fluorescence.<sup>22</sup> For preventing organic dyes from separating from oils the mixtures may be stabilized by addition of water insoluble soaps, such as fatty or resinous soaps of zinc, calcium, magnesium, or aluminum.<sup>23</sup> However, addition of fluorescence agents is not absolutely necessary for imparting to oils the yellowish-green bloom characteristic of Pennsylvania oils. Sufficient improvement may be frequently obtained by contacting oils with clay at elevated temperatures, by treating oils with sulfuric acid in propane solution, or by other conventional refining methods.

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# Appendix

TABLE I—Gravity—Weight—Volume Conversion Tables

(From R. E. Leigh, Refiner, Dec. 1931, 106-7).

| Degrees<br>A.P.I. | Specific<br>Gravity | Pounds<br>Per<br>Gallon | Gallons<br>Per<br>Pound | Barrels<br>Per<br>Long<br>Ton | Barrels<br>Per<br>Metric<br>Ton | Cubic<br>Meters<br>Per<br>Long<br>Ton | Cubic<br>Meters<br>Per<br>Metric<br>Ton |
|-------------------|---------------------|-------------------------|-------------------------|-------------------------------|---------------------------------|---------------------------------------|---|
| 10.0              | 1.0000              | 8.328                   | 0.1201                  | 6.4041                        | 6.3030                          | 1.01729                               | 1.00123                                 |
| 10.5              | 0.9965              | 8.299                   | 0.1205                  | 6.4265                        | 6.3250                          | 1.02085                               | 1.00472                                 |
| 11.0              | 0.9930              | 8.270                   | 0.1209                  | 6.4490                        | 6.3472                          | 1.02443                               | 1.00825                                 |
| 11.5              | 0.9895              | 8.241                   | 0.1213                  | 6.4717                        | 6.3695                          | 1.02803                               | 1.01180                                 |
| 12.0              | 0.9861              | 8.212                   | 0.1218                  | 6.4946                        | 6.3920                          | 1.03166                               | 1.01537                                 |
| 12.5              | 0.9826              | 8.183                   | 0.1222                  | 6.5176                        | 6.4146                          | 1.03532                               | 1.01897                                 |
| 13.0              | 0.9792              | 8.155                   | 0.1226                  | 6.5400                        | 6.4367                          | 1.03887                               | 1.02246                                 |
| 13.5              | 0.9759              | 8.127                   | 0.1230                  | 6.5625                        | 6.4588                          | 1.04245                               | 1.02599                                 |
| 14.0              | 0.9725              | 8.099                   | 0.1235                  | 6.5852                        | 6.4812                          | 1.04606                               | 1.02954                                 |
| 14.5              | 0.9692              | 8.071                   | 0.1239                  | 6.6080                        | 6.5037                          | 1.04969                               | 1.03311                                 |
| 15.0              | 0.9659              | 8.044                   | 0.1243                  | 6.6302                        | 6.5255                          | 1.05321                               | 1.03657                                 |
| 15.5              | 0.9626              | 8.016                   | 0.1248                  | 6.6534                        | 6.5483                          | 1.05689                               | 1.04020                                 |
| 16.0              | 0.9593              | 7.989                   | 0.1252                  | 6.6758                        | 6.5704                          | 1.06046                               | 1.04371                                 |
| 16.5              | 0.9561              | 7.962                   | 0.1256                  | 6.6985                        | 6.5927                          | 1.06406                               | 1.04725                                 |
| 17.0              | 0.9529              | 7.935                   | 0.1260                  | 6.7213                        | 6.6151                          | 1.06768                               | 1.05081                                 |
| 17.5              | 0.9497              | 7.909                   | 0.1264                  | 6.7434                        | 6.6369                          | 1.07119                               | 1.05427                                 |
| 18.0              | 0.9465              | 7.882                   | 0.1269                  | 6.7665                        | 6.6596                          | 1.07486                               | 1.05788                                 |
| 18.5              | 0.9433              | 7.856                   | 0.1273                  | 6.7889                        | 6.6816                          | 1.07841                               | 1.06138                                 |
| 19.0              | 0.9402              | 7.830                   | 0.1277                  | 6.8114                        | 6.7038                          | 1.08199                               | 1.06490                                 |
| 19.5              | 0.9371              | 7.804                   | 0.1281                  | 6.8341                        | 6.7262                          | 1.08560                               | 1.06845                                 |
| 20.0              | 0.9340              | 7.778                   | 0.1286                  | 6.8569                        | 6.7487                          | 1.08923                               | 1.07202                                 |
| 20.5              | 0.9309              | 7.752                   | 0.1290                  | 6.8799                        | 6.7712                          | 1.09288                               | 1.07562                                 |
| 21.0              | 0.9279              | 7.727                   | 0.1294                  | 6.9022                        | 6.7932                          | 1.09642                               | 1.07910                                 |
| 21.5              | 0.9248              | 7.701                   | 0.1299                  | 6.9255                        | 6.8161                          | 1.10012                               | 1.08274                                 |
| 22.0              | 0.9218              | 7.676                   | 0.1303                  | 6.9481                        | 6.8383                          | 1.10370                               | 1.08627                                 |
| 22.5              | 0.9188              | 7.651                   | 0.1307                  | 6.9708                        | 6.8607                          | 1.10731                               | 1.08982                                 |
| 23.0              | 0.9159              | 7.627                   | 0.1311                  | 6.9927                        | 6.8823                          | 1.11079                               | 1.09325                                 |
| 23.5              | 0.9129              | 7.602                   | 0.1315                  | 7.0157                        | 6.9048                          | 1.11445                               | 1.09684                                 |
| 24.0              | 0.9100              | 7.578                   | 0.1320                  | 7.0379                        | 6.9268                          | 1.11797                               | 1.10032                                 |
| 24.5              | 0.9071              | 7.554                   | 0.1324                  | 7.0603                        | 6.9488                          | 1.12153                               | 1.10381                                 |
| 25.0              | 0.9042              | 7.529                   | 0.1328                  | 7.0837                        | 6.9718                          | 1.12525                               | 1.10748                                 |
| 25.5              | 0.9013              | 7.505                   | 0.1332                  | 7.1064                        | 6.9941                          | 1.12885                               | 1.11102                                 |
| 26.0              | 0.8984              | 7.481                   | 0.1337                  | 7.1292                        | 7.0166                          | 1.13247                               | 1.11458                                 |
| 26.5              | 0.8956              | 7.458                   | 0.1341                  | 7.1512                        | 7.0382                          | 1.13596                               | 1.11802                                 |
| 27.0              | 0.8927              | 7.434                   | 0.1345                  | 7.1742                        | 7.0609                          | 1.13963                               | 1.12163                                 |
| 27.5              | 0.8899              | 7.410                   | 0.1350                  | 7.1975                        | 7.0838                          | 1.14332                               | 1.12526                                 |
| 28.0              | 0.8871              | 7.387                   | 0.1354                  | 7.2199                        | 7.1059                          | 1.14688                               | 1.12877                                 |
| 28.5              | 0.8844              | 7.364                   | 0.1358                  | 7.2424                        | 7.1281                          | 1.15046                               | 1.13229                                 |
| 29.0              | 0.8816              | 7.341                   | 0.1362                  | 7.2651                        | 7.1504                          | 1.15407                               | 1.13584                                 |
| 29.5              | 0.8789              | 7.318                   | 0.1366                  | 7.2880                        | 7.1729                          | 1.15770                               | 1.13941                                 |
| 30.0              | 0.8762              | 7.296                   | 0.1371                  | 7.3099                        | 7.1945                          | 1.16119                               | 1.14285                                 |
| 30.5              | 0.8735              | 7.273                   | 0.1375                  | 7.3331                        | 7.2172                          | 1.16486                               | 1.14646                                 |
| 31.0              | 0.8708              | 7.251                   | 0.1379                  | 7.3553                        | 7.2391                          | 1.16839                               | 1.14994                                 |
| 31.5              | 0.8681              | 7.228                   | 0.1384                  | 7.3787                        | 7.2622                          | 1.17211                               | 1.15360                                 |
| 32.0              | 0.8654              | 7.206                   | 0.1388                  | 7.4012                        | 7.2843                          | 1.17569                               | 1.15712                                 |
| 32.5              | 0.8628              | 7.184                   | 0.1392                  | 7.4239                        | 7.3067                          | 1.17929                               | 1.16066                                 |
| 33.0              | 0.8602              | 7.163                   | 0.1396                  | 7.4457                        | 7.3281                          | 1.18275                               | 1.16407                                 |
| 33.5              | 0.8576              | 7.141                   | 0.1400                  | 7.4686                        | 7.3507                          | 1.18639                               | 1.16765                                 |
| 34.0              | 0.8550              | 7.119                   | 0.1405                  | 7.4917                        | 7.3734                          | 1.19006                               | 1.17126                                 |
| 34.5              | 0.8524              | 7.098                   | 0.1409                  | 7.5139                        | 7.3952                          | 1.19359                               | 1.17473                                 |
| 35.0              | 0.8498              | 7.076                   | 0.1413                  | 7.5372                        | 7.4182                          | 1.19729                               | 1.17838                                 |
| 35.5              | 0.8473              | 7.055                   | 0.1417                  | 7.5597                        | 7.4403                          | 1.20085                               | 1.18189                                 |
| 36.0              | 0.8448              | 7.034                   | 0.1422                  | 7.5822                        | 7.4625                          | 1.20444                               | 1.18541                                 |
| 36.5              | 0.8423              | 7.013                   | 0.1426                  | 7.6049                        | 7.4848                          | 1.20804                               | 1.18896                                 |
| 37.0              | 0.8398              | 6.993                   | 0.1430                  | 7.6266                        | 7.5062                          | 1.21150                               | 1.19237                                 |
| 37.5              | 0.8373              | 6.972                   | 0.1434                  | 7.6496                        | 7.5288                          | 1.21515                               | 1.19596                                 |
| 38.0              | 0.8348              | 6.951                   | 0.1439                  | 7.6728                        | 7.5516                          | 1.21882                               | 1.19957                                 |
| 38.5              | 0.8324              | 6.930                   | 0.1443                  | 7.6960                        | 7.5745                          | 1.22251                               | 1.20320                                 |
| 39.0              | 0.8299              | 6.910                   | 0.1447                  | 7.7183                        | 7.5964                          | 1.22605                               | 1.20669                                 |
| 39.5              | 0.8275              | 6.890                   | 0.1451                  | 7.7407                        | 7.6184                          | 1.22961                               | 1.21019                                 |

TABLE I—(Continued)

| Degrees<br>A.P.I. | Specific<br>Gravity | Pounds<br>Per<br>Gallon | Gallons<br>Per<br>Pound | Barrels<br>Per<br>Long<br>Ton | Barrels<br>Per<br>Metric<br>Ton | Cubic<br>Meters<br>Per<br>Long<br>Ton | Cubic<br>Meters<br>Per<br>Metric<br>Ton |
|-------------------|---------------------|-------------------------|-------------------------|-------------------------------|---------------------------------|---------------------------------------|---|
| 40.0              | 0.8251              | 6.870                   | 0.1456                  | 7.7632                        | 7.6406                          | 1.23319                               | 1.21371                                 |
| 40.5              | 0.8227              | 6.850                   | 0.1460                  | 7.7859                        | 7.6629                          | 1.23679                               | 1.21726                                 |
| 41.0              | 0.8203              | 6.830                   | 0.1464                  | 7.8087                        | 7.6854                          | 1.24041                               | 1.22082                                 |
| 41.5              | 0.8179              | 6.810                   | 0.1468                  | 7.8316                        | 7.7079                          | 1.24405                               | 1.22441                                 |
| 42.0              | 0.8155              | 6.790                   | 0.1473                  | 7.8547                        | 7.7306                          | 1.24772                               | 1.22801                                 |
| 42.5              | 0.8132              | 6.771                   | 0.1477                  | 7.8767                        | 7.7523                          | 1.25122                               | 1.23146                                 |
| 43.0              | 0.8109              | 6.752                   | 0.1481                  | 7.8989                        | 7.7741                          | 1.25474                               | 1.23492                                 |
| 43.5              | 0.8086              | 6.732                   | 0.1485                  | 7.9224                        | 7.7972                          | 1.25847                               | 1.23859                                 |
| 44.0              | 0.8063              | 6.713                   | 0.1490                  | 7.9448                        | 7.8193                          | 1.26203                               | 1.24210                                 |
| 44.5              | 0.8040              | 6.694                   | 0.1494                  | 7.9673                        | 7.8415                          | 1.26561                               | 1.24562                                 |
| 45.0              | 0.8017              | 6.675                   | 0.1498                  | 7.9900                        | 7.8638                          | 1.26921                               | 1.24917                                 |
| 45.5              | 0.7994              | 6.656                   | 0.1502                  | 8.0128                        | 7.8863                          | 1.27284                               | 1.25274                                 |
| 46.0              | 0.7972              | 6.637                   | 0.1507                  | 8.0358                        | 7.9088                          | 1.27648                               | 1.25632                                 |
| 46.5              | 0.7949              | 6.618                   | 0.1511                  | 8.0588                        | 7.9316                          | 1.28015                               | 1.25993                                 |
| 47.0              | 0.7927              | 6.600                   | 0.1515                  | 8.0808                        | 7.9532                          | 1.28364                               | 1.26336                                 |
| 47.5              | 0.7905              | 6.582                   | 0.1519                  | 8.1029                        | 7.9749                          | 1.28715                               | 1.26682                                 |
| 48.0              | 0.7883              | 6.563                   | 0.1524                  | 8.1264                        | 7.9980                          | 1.29087                               | 1.27049                                 |
| 48.5              | 0.7861              | 6.545                   | 0.1528                  | 8.1487                        | 8.0200                          | 1.29443                               | 1.27398                                 |
| 49.0              | 0.7839              | 6.526                   | 0.1532                  | 8.1724                        | 8.0434                          | 1.29819                               | 1.27769                                 |
| 49.5              | 0.7818              | 6.509                   | 0.1536                  | 8.1938                        | 8.0644                          | 1.30158                               | 1.28103                                 |
| 50.0              | 0.7796              | 6.490                   | 0.1541                  | 8.2178                        | 8.0880                          | 1.30539                               | 1.28478                                 |
| 50.5              | 0.7775              | 6.473                   | 0.1545                  | 8.2394                        | 8.1092                          | 1.30882                               | 1.28815                                 |
| 51.0              | 0.7753              | 6.455                   | 0.1549                  | 8.2623                        | 8.1318                          | 1.31247                               | 1.29174                                 |
| 51.5              | 0.7732              | 6.437                   | 0.1554                  | 8.2854                        | 8.1546                          | 1.31614                               | 1.29536                                 |
| 52.0              | 0.7711              | 6.420                   | 0.1558                  | 8.3074                        | 8.1762                          | 1.31963                               | 1.29879                                 |
| 52.5              | 0.7690              | 6.402                   | 0.1562                  | 8.3307                        | 8.1992                          | 1.32334                               | 1.30244                                 |
| 53.0              | 0.7669              | 6.385                   | 0.1566                  | 8.3529                        | 8.2210                          | 1.32686                               | 1.30591                                 |
| 53.5              | 0.7649              | 6.368                   | 0.1570                  | 8.3752                        | 8.2429                          | 1.33040                               | 1.30939                                 |
| 54.0              | 0.7628              | 6.350                   | 0.1575                  | 8.3990                        | 8.2663                          | 1.33418                               | 1.31310                                 |
| 54.5              | 0.7608              | 6.334                   | 0.1579                  | 8.4202                        | 8.2872                          | 1.33755                               | 1.31642                                 |
| 55.0              | 0.7587              | 6.316                   | 0.1583                  | 8.4442                        | 8.3108                          | 1.34136                               | 1.32017                                 |
| 55.5              | 0.7567              | 6.300                   | 0.1587                  | 8.4656                        | 8.3319                          | 1.34476                               | 1.32353                                 |
| 56.0              | 0.7547              | 6.283                   | 0.1592                  | 8.4885                        | 8.3544                          | 1.34840                               | 1.32711                                 |
| 56.5              | 0.7527              | 6.266                   | 0.1596                  | 8.5115                        | 8.3771                          | 1.35206                               | 1.33071                                 |
| 57.0              | 0.7507              | 6.249                   | 0.1600                  | 8.5347                        | 8.3999                          | 1.35574                               | 1.33433                                 |
| 57.5              | 0.7487              | 6.233                   | 0.1604                  | 8.5566                        | 8.4215                          | 1.35922                               | 1.33775                                 |
| 58.0              | 0.7467              | 6.216                   | 0.1609                  | 8.5800                        | 8.4445                          | 1.36294                               | 1.34141                                 |
| 58.5              | 0.7447              | 6.199                   | 0.1613                  | 8.6035                        | 8.4677                          | 1.36667                               | 1.34509                                 |
| 59.0              | 0.7428              | 6.184                   | 0.1617                  | 8.6244                        | 8.4882                          | 1.36999                               | 1.34835                                 |
| 59.5              | 0.7408              | 6.167                   | 0.1622                  | 8.6482                        | 8.5116                          | 1.37377                               | 1.35207                                 |
| 60.0              | 0.7389              | 6.151                   | 0.1626                  | 8.6707                        | 8.5338                          | 1.37734                               | 1.35559                                 |
| 60.5              | 0.7370              | 6.135                   | 0.1630                  | 8.6933                        | 8.5560                          | 1.38093                               | 1.35912                                 |
| 61.0              | 0.7351              | 6.119                   | 0.1634                  | 8.7160                        | 8.5784                          | 1.38454                               | 1.36268                                 |
| 61.5              | 0.7332              | 6.103                   | 0.1639                  | 8.7389                        | 8.6009                          | 1.38817                               | 1.36625                                 |
| 62.0              | 0.7313              | 6.087                   | 0.1643                  | 8.7618                        | 8.6235                          | 1.39182                               | 1.36984                                 |
| 62.5              | 0.7294              | 6.072                   | 0.1647                  | 8.7835                        | 8.6448                          | 1.39526                               | 1.37322                                 |
| 63.0              | 0.7275              | 6.056                   | 0.1651                  | 8.8067                        | 8.6676                          | 1.39895                               | 1.37685                                 |
| 63.5              | 0.7256              | 6.040                   | 0.1656                  | 8.8300                        | 8.6906                          | 1.40265                               | 1.38050                                 |
| 64.0              | 0.7238              | 6.025                   | 0.1660                  | 8.8520                        | 8.7122                          | 1.40614                               | 1.38394                                 |
| 64.5              | 0.7219              | 6.010                   | 0.1664                  | 8.8741                        | 8.7339                          | 1.40965                               | 1.38739                                 |
| 65.0              | 0.7201              | 5.994                   | 0.1668                  | 8.8978                        | 8.7573                          | 1.41342                               | 1.39109                                 |
| 65.5              | 0.7183              | 5.979                   | 0.1673                  | 8.9201                        | 8.7792                          | 1.41696                               | 1.39458                                 |
| 66.0              | 0.7165              | 5.964                   | 0.1677                  | 8.9425                        | 8.8013                          | 1.42053                               | 1.39809                                 |
| 66.5              | 0.7146              | 5.949                   | 0.1681                  | 8.9651                        | 8.8235                          | 1.42411                               | 1.40162                                 |
| 67.0              | 0.7128              | 5.934                   | 0.1685                  | 8.9878                        | 8.8458                          | 1.42771                               | 1.40516                                 |
| 67.5              | 0.7111              | 5.919                   | 0.1689                  | 9.0105                        | 8.8682                          | 1.43132                               | 1.40872                                 |
| 68.0              | 0.7093              | 5.904                   | 0.1694                  | 9.0334                        | 8.8908                          | 1.43496                               | 1.41230                                 |
| 68.5              | 0.7075              | 5.889                   | 0.1698                  | 9.0564                        | 8.9134                          | 1.43861                               | 1.41590                                 |
| 69.0              | 0.7057              | 5.874                   | 0.1702                  | 9.0796                        | 8.9362                          | 1.44229                               | 1.41951                                 |
| 69.5              | 0.7040              | 5.860                   | 0.1706                  | 9.1013                        | 8.9575                          | 1.44574                               | 1.42290                                 |

TABLE I—(Continued)

| Degrees<br>A.P.I. | Specific<br>Gravity | Pounds<br>Per<br>Gallon | Gallons<br>Per<br>Pound | Barrels<br>Per<br>Long<br>Ton | Barrels<br>Per<br>Metric<br>Ton | Cubic<br>Meters<br>Per<br>Long<br>Ton | Cubic<br>Meters<br>Per<br>Metric<br>Ton |
|-------------------|---------------------|-------------------------|-------------------------|-------------------------------|---------------------------------|---------------------------------------|---|
| 70.0              | 0.7022              | 5.845                   | 0.1711                  | 9.1246                        | 8.9805                          | 1.44945                               | 1.42655                                 |
| 70.5              | 0.7005              | 5.831                   | 0.1715                  | 9.1465                        | 9.0021                          | 1.45293                               | 1.42998                                 |
| 71.0              | 0.6988              | 5.817                   | 0.1719                  | 9.1685                        | 9.0237                          | 1.45642                               | 1.43342                                 |
| 71.5              | 0.6970              | 5.802                   | 0.1724                  | 9.1922                        | 9.0471                          | 1.46019                               | 1.43713                                 |
| 72.0              | 0.6953              | 5.788                   | 0.1728                  | 9.2145                        | 9.0689                          | 1.46372                               | 1.44060                                 |
| 72.5              | 0.6936              | 5.773                   | 0.1732                  | 9.2384                        | 9.0925                          | 1.46752                               | 1.44435                                 |
| 73.0              | 0.6919              | 5.759                   | 0.1736                  | 9.2609                        | 9.1146                          | 1.47109                               | 1.44786                                 |
| 73.5              | 0.6902              | 5.745                   | 0.1741                  | 9.2834                        | 9.1368                          | 1.47468                               | 1.45139                                 |
| 74.0              | 0.6886              | 5.731                   | 0.1745                  | 9.3061                        | 9.1591                          | 1.47828                               | 1.45493                                 |
| 74.5              | 0.6869              | 5.718                   | 0.1749                  | 9.3273                        | 9.1800                          | 1.48164                               | 1.45824                                 |
| 75.0              | 0.6852              | 5.703                   | 0.1753                  | 9.3518                        | 9.2041                          | 1.48554                               | 1.46207                                 |
| 75.5              | 0.6836              | 5.690                   | 0.1757                  | 9.3732                        | 9.2251                          | 1.48893                               | 1.46541                                 |
| 76.0              | 0.6819              | 5.676                   | 0.1762                  | 9.3963                        | 9.2479                          | 1.49260                               | 1.46903                                 |
| 76.5              | 0.6803              | 5.662                   | 0.1766                  | 9.4195                        | 9.2708                          | 1.49629                               | 1.47266                                 |
| 77.0              | 0.6787              | 5.649                   | 0.1770                  | 9.4412                        | 9.2921                          | 1.49974                               | 1.47605                                 |
| 77.5              | 0.6770              | 5.635                   | 0.1775                  | 9.4647                        | 9.3152                          | 1.50346                               | 1.47972                                 |
| 78.0              | 0.6754              | 5.522                   | 0.1779                  | 9.4865                        | 9.3367                          | 1.50694                               | 1.48314                                 |
| 78.5              | 0.6738              | 5.608                   | 0.1783                  | 9.5102                        | 9.3600                          | 1.51070                               | 1.48684                                 |
| 79.0              | 0.6722              | 5.595                   | 0.1787                  | 9.5323                        | 9.3818                          | 1.51421                               | 1.49030                                 |
| 79.5              | 0.6706              | 5.582                   | 0.1791                  | 9.5545                        | 9.4036                          | 1.51774                               | 1.49377                                 |
| 80.0              | 0.6690              | 5.568                   | 0.1796                  | 9.5785                        | 9.4273                          | 1.52155                               | 1.49752                                 |
| 80.5              | 0.6675              | 5.556                   | 0.1800                  | 9.5992                        | 9.4476                          | 1.52484                               | 1.50076                                 |
| 81.0              | 0.6659              | 5.542                   | 0.1804                  | 9.6235                        | 9.4715                          | 1.52869                               | 1.50455                                 |
| 81.5              | 0.6643              | 5.529                   | 0.1809                  | 9.6461                        | 9.4938                          | 1.53229                               | 1.50809                                 |
| 82.0              | 0.6628              | 5.516                   | 0.1813                  | 9.6688                        | 9.5161                          | 1.53590                               | 1.51164                                 |
| 82.5              | 0.6612              | 5.503                   | 0.1817                  | 9.6917                        | 9.5386                          | 1.53953                               | 1.51521                                 |
| 83.0              | 0.6597              | 5.491                   | 0.1821                  | 9.7129                        | 9.5595                          | 1.54289                               | 1.51852                                 |
| 83.5              | 0.6581              | 5.477                   | 0.1826                  | 9.7377                        | 9.5839                          | 1.54683                               | 1.52240                                 |
| 84.0              | 0.6566              | 5.465                   | 0.1830                  | 9.7591                        | 9.6049                          | 1.55023                               | 1.52575                                 |
| 84.5              | 0.6551              | 5.453                   | 0.1834                  | 9.7805                        | 9.6261                          | 1.55364                               | 1.52910                                 |
| 85.0              | 0.6536              | 5.440                   | 0.1838                  | 9.8039                        | 9.6491                          | 1.55736                               | 1.53276                                 |
| 85.5              | 0.6521              | 5.427                   | 0.1843                  | 9.8274                        | 9.6722                          | 1.56109                               | 1.53643                                 |
| 86.0              | 0.6506              | 5.415                   | 0.1847                  | 9.8492                        | 9.6936                          | 1.56455                               | 1.53984                                 |
| 86.5              | 0.6491              | 5.402                   | 0.1851                  | 9.8729                        | 9.7170                          | 1.56831                               | 1.54354                                 |
| 87.0              | 0.6476              | 5.390                   | 0.1855                  | 9.8949                        | 9.7386                          | 1.57180                               | 1.54698                                 |
| 87.5              | 0.6461              | 5.377                   | 0.1860                  | 9.9188                        | 9.7621                          | 1.57560                               | 1.55072                                 |
| 88.0              | 0.6446              | 5.365                   | 0.1864                  | 9.9410                        | 9.7840                          | 1.57913                               | 1.55419                                 |
| 88.5              | 0.6432              | 5.353                   | 0.1868                  | 9.9633                        | 9.8059                          | 1.58267                               | 1.55767                                 |
| 89.0              | 0.6417              | 5.341                   | 0.1872                  | 9.9856                        | 9.8279                          | 1.58622                               | 1.56117                                 |
| 89.5              | 0.6403              | 5.329                   | 0.1877                  | 10.0081                       | 9.8501                          | 1.58979                               | 1.56469                                 |
| 90.0              | 0.6388              | 5.316                   | 0.1881                  | 10.0326                       | 9.8742                          | 1.59368                               | 1.56851                                 |
| 90.5              | 0.6374              | 5.305                   | 0.1885                  | 10.0534                       | 9.8946                          | 1.59699                               | 1.57176                                 |
| 91.0              | 0.6360              | 5.293                   | 0.1889                  | 10.0762                       | 9.9171                          | 1.60061                               | 1.57533                                 |
| 91.5              | 0.6345              | 5.281                   | 0.1894                  | 10.0991                       | 9.9396                          | 1.60424                               | 1.57891                                 |
| 92.0              | 0.6331              | 5.269                   | 0.1898                  | 10.1221                       | 9.9622                          | 1.60790                               | 1.58250                                 |
| 92.5              | 0.6317              | 5.257                   | 0.1902                  | 10.1452                       | 9.9850                          | 1.61157                               | 1.58612                                 |
| 93.0              | 0.6303              | 5.246                   | 0.1906                  | 10.1665                       | 10.0059                         | 1.61495                               | 1.58944                                 |
| 93.5              | 0.6289              | 5.234                   | 0.1911                  | 10.1898                       | 10.0289                         | 1.61865                               | 1.59309                                 |
| 94.0              | 0.6275              | 5.222                   | 0.1915                  | 10.2132                       | 10.0519                         | 1.62237                               | 1.59675                                 |
| 94.5              | 0.6261              | 5.210                   | 0.1919                  | 10.2367                       | 10.0750                         | 1.62611                               | 1.60042                                 |
| 95.0              | 0.6247              | 5.199                   | 0.1924                  | 10.2584                       | 10.0964                         | 1.62955                               | 1.60381                                 |
| 95.5              | 0.6233              | 5.187                   | 0.1928                  | 10.2821                       | 10.1197                         | 1.63332                               | 1.60752                                 |
| 96.0              | 0.6220              | 5.176                   | 0.1932                  | 10.3040                       | 10.1412                         | 1.63679                               | 1.61094                                 |
| 96.5              | 0.6206              | 5.164                   | 0.1936                  | 10.3279                       | 10.1648                         | 1.64059                               | 1.61468                                 |
| 97.0              | 0.6193              | 5.154                   | 0.1940                  | 10.3479                       | 10.1845                         | 1.64377                               | 1.61781                                 |
| 97.5              | 0.6179              | 5.142                   | 0.1945                  | 10.3721                       | 10.2083                         | 1.64761                               | 1.62159                                 |
| 98.0              | 0.6166              | 5.131                   | 0.1949                  | 10.3943                       | 10.2302                         | 1.65114                               | 1.62506                                 |
| 98.5              | 0.6152              | 5.120                   | 0.1953                  | 10.4167                       | 10.2521                         | 1.65469                               | 1.62856                                 |
| 99.0              | 0.6139              | 5.109                   | 0.1957                  | 10.4391                       | 10.2742                         | 1.65825                               | 1.63206                                 |
| 99.5              | 0.6126              | 5.098                   | 0.1962                  | 10.4616                       | 10.2964                         | 1.66183                               | 1.63558                                 |
| 100.0             | 0.6112              | 5.086                   | 0.1966                  | 10.4863                       | 10.3207                         | 1.66575                               | 1.63944                                 |

TABLE II—Approximate Viscosity Conversion Equations

General equations for converting viscosity readings of commercial viscosimeters to absolute viscosities are of the following type:

$$\frac{V}{d} = aT - \frac{b}{T}$$

where:  $V$  = absolute viscosity,  
 $d$  = density of the oil at the temperature at which the viscosity is being measured,  
 $T$  = reading of commercial instruments,  
 $a$  and  $b$  = constants.

| Viscometer         | Range             | a       | b      |
|--------------------|-------------------|---------|--------|
| Saybolt Universal  | 32-145 seconds    | 0.00226 | 1.95   |
| Saybolt Universal  | above 145 seconds | 0.00220 | 0.8    |
| Saybolt Furol      | 25-40 seconds     | 0.0224  | 1.84   |
| Saybolt Furol      | above 40 seconds  | 0.0216  | 0.6    |
| Redwood Standard   | below 100 seconds | 0.0026  | 1.79   |
| Redwood Standard   | above 100 seconds | 0.00247 | 0.5    |
| Admiralty Fuel Oil | above 100 seconds | 0.0247  | 0.0(1) |
| Engler             | 1.35-3.2 degrees  | 0.08    | 0.0864 |
| Engler             | above 3.2 degrees | 0.076   | 0.04   |

(1) Admiralty Fuel Oil Viscometer should be used on oils having viscosities greater than 1000 Redwood Standard seconds.

The conversions are only approximate and should not be used when considerable accuracy is required.

[From F. H. Garner and C. I. Kelly, *Physics* 4, 97-112 (1933).]

TABLE III—Tables for Calculating Viscosity Index of Lubricating Oils

| S.U.V.<br>210° F. | L    | D   | S.U.V.<br>210° F. | L    | D    | S.U.V.<br>210° F. | L    | D    |
|-------------------|------|-----|-------------------|------|------|-------------------|------|------|
| 40                | 138  | 31  | 80                | 1627 | 836  | 120               | 3838 | 2218 |
| 41                | 161  | 41  | 81                | 1674 | 864  | 121               | 3902 | 2259 |
| 42                | 185  | 52  | 82                | 1721 | 892  | 122               | 3966 | 2301 |
| 43                | 210  | 63  | 83                | 1769 | 920  | 123               | 4031 | 2343 |
| 44                | 237  | 76  | 84                | 1817 | 949  | 124               | 4097 | 2387 |
| 45                | 265  | 89  | 85                | 1865 | 977  | 125               | 4163 | 2430 |
| 46                | 293  | 102 | 86                | 1914 | 1007 | 126               | 4229 | 2473 |
| 47                | 322  | 116 | 87                | 1964 | 1037 | 127               | 4296 | 2517 |
| 48                | 353  | 131 | 88                | 2014 | 1067 | 128               | 4363 | 2561 |
| 49                | 386  | 147 | 89                | 2064 | 1098 | 129               | 4430 | 2605 |
| 50                | 422  | 165 | 90                | 2115 | 1129 | 130               | 4498 | 2650 |
| 51                | 456  | 184 | 91                | 2166 | 1160 | 131               | 4567 | 2696 |
| 52                | 491  | 202 | 92                | 2217 | 1191 | 132               | 4636 | 2742 |
| 53                | 525  | 220 | 93                | 2270 | 1224 | 133               | 4705 | 2787 |
| 54                | 560  | 238 | 94                | 2322 | 1256 | 134               | 4775 | 2834 |
| 55                | 596  | 257 | 95                | 2375 | 1288 | 135               | 4845 | 2880 |
| 56                | 632  | 276 | 96                | 2428 | 1321 | 136               | 4915 | 2927 |
| 57                | 669  | 295 | 97                | 2481 | 1353 | 137               | 4986 | 2974 |
| 58                | 706  | 315 | 98                | 2536 | 1388 | 138               | 5053 | 3022 |
| 59                | 743  | 335 | 99                | 2591 | 1423 | 139               | 5130 | 3070 |
| 60                | 781  | 355 | 100               | 2646 | 1457 | 140               | 5202 | 3118 |
| 61                | 819  | 376 | 101               | 2701 | 1491 | 141               | 5275 | 3167 |
| 62                | 857  | 397 | 102               | 2757 | 1526 | 142               | 5348 | 3216 |
| 63                | 897  | 418 | 103               | 2814 | 1562 | 143               | 5422 | 3266 |
| 64                | 936  | 440 | 104               | 2870 | 1597 | 144               | 5496 | 3316 |
| 65                | 976  | 462 | 105               | 2928 | 1634 | 145               | 5570 | 3365 |
| 66                | 1016 | 484 | 106               | 2985 | 1670 | 146               | 5645 | 3416 |
| 67                | 1057 | 507 | 107               | 3043 | 1706 | 147               | 5721 | 3467 |
| 68                | 1098 | 531 | 108               | 3102 | 1744 | 148               | 5796 | 3518 |
| 69                | 1140 | 554 | 109               | 3161 | 1782 | 149               | 5873 | 3570 |
| 70                | 1182 | 578 | 110               | 3220 | 1819 | 150               | 5949 | 3621 |
| 71                | 1225 | 602 | 111               | 3280 | 1858 | 151               | 6026 | 3673 |
| 72                | 1268 | 627 | 112               | 3340 | 1896 | 152               | 6104 | 3726 |
| 73                | 1311 | 652 | 113               | 3400 | 1934 | 153               | 6182 | 3779 |
| 74                | 1355 | 677 | 114               | 3462 | 1974 | 154               | 6260 | 3832 |
| 75                | 1399 | 702 | 115               | 3524 | 2014 | 155               | 6339 | 3886 |
| 76                | 1444 | 728 | 116               | 3585 | 2053 | 156               | 6418 | 3940 |
| 77                | 1489 | 755 | 117               | 3648 | 2094 | 157               | 6498 | 3995 |
| 78                | 1534 | 781 | 118               | 3711 | 2135 | 158               | 6578 | 4049 |
| 79                | 1580 | 808 | 119               | 3774 | 2176 | 159               | 6659 | 4105 |
|                   |      |     |                   |      |      | 160               | 6740 | 4160 |

$$\text{Viscosity index} = \frac{L - U}{D} \times 100$$

$L$  = S.U.V. at 100° F. of low viscosity index oil of X sec. at 210° F.

$D$  = difference in S.U.V. at 100° F. between low and high viscosity index oils of X sec. at 210° F.

$U$  = S.U.V. at 100° F. of unknown viscosity index oil of X sec. at 210° F.

TABLE IV—Approximate Color Conversion Table

| N.P.A. | A.S.T.M. Grading<br>N.P.A. Name | Union | Tag<br>Robinson | Lovibond<br>$\frac{1}{2}$ " Cell | True<br>Color |
|--------|---------------------------------|-------|-----------------|----------------------------------|---------------|
| 1.0    | Lily White                      | G     | 21              | 0.4                              | 0.4           |
| 1.5    | Cream White                     | H     | 17.5            | 1.5                              | 1.5           |
| 2.0    | Extra Pale                      | I     | 12.5            | 5.5                              | 5.5           |
| 2.5    | Extra Lemon Pale                | J     | 10.25           | 10                               | 10            |
| 3.0    | Lemon Pale                      | K     | 9.75            | 14                               | 14            |
| 3.5    | Extra Orange Pale               | L     | 9.25            | 20                               | 20            |
| 4.0    | Orange Pale                     | M     | 8.25            | 32                               | 32            |
| 4.5    | Pale                            | N     | 5.75            | 42                               | 42            |
| 5.0    | Light Red                       | O     | 3.50            | 55                               | 56            |
| 6.0    | Dark Red                        | P     | 2.25            | 90                               | 100           |
| 7.0    | Claret Red                      | Q     | 1.50            | 135                              | 170           |
| 8.0    | Extra Dark Red                  | R     | ....            | 200                              | 285           |
| A      | Extra Light Filtered            | A     | ....            | ...                              | ...           |
| D      | Light Filtered                  | D     | ....            | ...                              | ...           |
| E      | Medium Filtered                 | E     | ....            | ...                              | ...           |

The data are only approximate as exact comparisons between the different commercial colorimeters are impossible for the reasons explained in Chapter I.

"True" colors are, approximately, additive although very considerable deviations might be expected for the explained reasons.

TABLE V—Empirical Equations for Thermal Properties of Petroleum Products

| Property  | Units  | Empirical Equation  | Experimental Range  |   | Estimated Accuracy, Per Cent   |
|---|--|---|---|---|--|
|   |  |   | $d$   | $t$   |  |
| In engineering units: $d$ = specific gravity at 60°/60° F.; $t$ = temperature in ° F.; $p$ = pressure in lbs./in. <sup>2</sup> absolute; unit volume of liquid = gallon, measured at 60° F. |  |   |   |   |  |
| Coefficient of expansion of liquid.   | $\frac{1}{V_{60}} \frac{dV}{dt}$   | $= .A + 2B(t - 60)$   | 0.51-1.00   | 32-200  | 5  |
| Total heat of combustion at constant volume.  | $\left\{ \begin{array}{l} \text{B.t.u./lb.} \\ \text{B.t.u./gal.} \end{array} \right.$           | $\log(.A \times 10^5) = 0.835 + \frac{0.70}{d}$<br>$\log(B \times 10^5) = \frac{2.10}{d}$<br>$= \frac{22,320 - 3,780d^2}{186,087d - 31,515d^2}$ | $\left. \begin{array}{l} 0.51-0.99 \\ \dots\dots\dots \end{array} \right\}$ | $\left. \begin{array}{l} 32-200 \\ \dots\dots\dots \end{array} \right\}$  | $\left. \begin{array}{l} 1 \\ \dots\dots\dots \end{array} \right\}$  |
| Specific volume of vapor.   | ft. <sup>3</sup> /lb.  | $= \frac{0.242(t + 460)}{(1.03 - d)}$   | 0.51-0.80   |   | 10   |
| Thermal conductivity of liquid.   | $\frac{\text{B.t.u. in.}}{\text{ft.2 hr. ° F.}}$   | $= \frac{0.813}{d} [1 - 0.0003(t - 32)]$  | 0.78-0.95   | 32-400  | 10   |
| Specific heat of liquid.  | $\left\{ \begin{array}{l} \text{B.t.u./lb. ° F.} \\ \text{B.t.u./gal. ° F.} \end{array} \right.$ | $= \frac{1}{\sqrt{d}} (0.388 + 0.00045t)$   | $\left. \begin{array}{l} 0.72-0.96 \\ \dots\dots\dots \end{array} \right\}$ | $\left. \begin{array}{l} 32-750 \\ \dots\dots\dots \end{array} \right\}$  | $\left. \begin{array}{l} 5 \\ \dots\dots\dots \end{array} \right\}$  |
| Latent heat of vaporization   | $\left\{ \begin{array}{l} \text{B.t.u./lb.} \\ \text{B.t.u./gal.} \end{array} \right.$           | $= \frac{1}{d} (110.9 - 0.09t)$   | $\left. \begin{array}{l} 0.64-0.91 \\ \dots\dots\dots \end{array} \right\}$ | $\left. \begin{array}{l} 100-600 \\ \dots\dots\dots \end{array} \right\}$ | $\left. \begin{array}{l} 10 \\ \dots\dots\dots \end{array} \right\}$ |
| Heat content of liquid.   | B.t.u./gal.  | $= 925 - 0.75t$   | 0.72-0.96   | 32-750  | 5  |
| Heat content of vapor.  | B.t.u./gal.  | $= \sqrt{d} (3.235t + 0.001875t^2 - 105.5)$   | 0.64-0.91   | 100-600   | 5  |

TABLE V—Empirical Equations for Thermal Properties of Petroleum Products—(Continued)

| Property  | Units  | Empirical Equation  | Experimental Range  |   | Estimated Accuracy, Per Cent                           |
|---|--|---|---|---|--|
|   |  |   | $d$   | $t$   |  |
| In metric units: $d$ = density in g./ml. at 15° C.; $t$ = temperature in °C.; $p$ = pressure in atmospheres; unit volume of liquid = milliliter, measured at 15° C. |  |   |   |   |  |
| Coefficient of expansion of liquid.   | $\frac{1}{V_{15}} \frac{dV}{dt}$   | $= A + 2B(t - 15)$  | 0.51–1.00   | 0–100   | 5  |
| Total heat of combustion at constant volume.  | $\left\{ \begin{array}{l} \text{Cal./g.} \\ \text{Cal./ml.} \end{array} \right.$                                   | $\log(A \times 10^5) = 1.09 + \frac{0.70}{d}$ ; $\log(B \times 10^5) = \frac{2.10}{d}$<br>$= 12,400 - 2,100d^2$<br>$= 12,400d - 2,100d^3$ | $\left. \begin{array}{l} 0.51-0.99 \\ 0.51-0.80 \end{array} \right\}$ | $\left. \begin{array}{l} \dots\dots\dots \\ \dots\dots\dots \end{array} \right\}$ | $\left. \begin{array}{l} 1 \\ 10 \end{array} \right\}$ |
| Specific volume of vapor....  | l/g.   | $\frac{0.821(t + 273)}{(1.03 - d)}$   | 0.51–0.80   |   | 10   |
| Thermal conductivity of liquid.   | $\frac{\text{Cal. cm.}}{\text{cm.}^2 \text{ sec. } ^\circ\text{C.}}$   | $\frac{p}{d}$<br>$= \frac{0.00028}{d} [1 - 0.00054t]$   | 0.78–0.95   | 0–200   | 10   |
| Specific heat of liquid.....  | $\left\{ \begin{array}{l} \text{Cal./g. } ^\circ\text{C.} \\ \text{Cal./ml. } ^\circ\text{C.} \end{array} \right.$ | $= \frac{1}{\sqrt{d}} (0.403 + 0.00081t)$<br>$= \sqrt{d} (0.403 + 0.00081t)$  | $\left. \begin{array}{l} 0.72-0.96 \\ 0.64-0.91 \end{array} \right\}$ | $\left. \begin{array}{l} 0-400 \\ 40-300 \end{array} \right\}$                    | $\left. \begin{array}{l} 5 \\ 10 \end{array} \right\}$ |
| Latent heat of vaporization   | $\left\{ \begin{array}{l} \text{Cal./g.} \\ \text{Cal./ml.} \end{array} \right.$                                   | $= \frac{1}{d} (60 - 0.09t)$<br>$= 60 - 0.09t$  | $\left. \begin{array}{l} 0.72-0.96 \\ 0.64-0.91 \end{array} \right\}$ | $\left. \begin{array}{l} 0-400 \\ 40-300 \end{array} \right\}$                    | $\left. \begin{array}{l} 5 \\ 5 \end{array} \right\}$  |
| Heat content of liquid.....   | Cal./ml.   | $= \sqrt{d} (0.403t + 0.000405t^2)$   | 0.72–0.96   | 0–400   | 5  |
| Heat content of vapor.....  | Cal./ml.   | $= 60 + (0.403\sqrt{d} - 0.09)t + 0.000405\sqrt{d}t^2$  | 0.64–0.91   | 40–300  | 5  |

[From C. S. Cragoe, Thermal Properties of Petroleum Products, Bur. of Standards, Misc. Publication 97 (1929).]

TABLE VI—Oxidation Tests

| Test                     | Temperature |      | Time<br>Hours  | Atmosphere | Catalyst | Size of<br>Sample |
|--------------------------|-------------|------|----------------|------------|----------|-------------------|
|                          | ° C.        | ° F. |                |            |          |                   |
| Anderson                 | 100         | 212  | 100            | Oxygen     | Cu+Fe    | 60 g.             |
| Belgian                  | 170         | 338  | 5              | Air        | None     | 40 c.c.           |
| British Air Ministry     | 200         | 392  | 24             | Air        | None     | 40 c.c.           |
| Brown-Boveri Transformer | 112         | 234  | 72/168         | Air        | Cu       | 1000 c.c.         |
| Brown-Boveri Turbine     | 110         | 230  | 72             | Air        | Cu       | 200 c.c.          |
| French                   | 150         | 302  | 5/50/125       | Air        | None     | 10 g.             |
| German Tar (Kissling)    | 120         | 248  | 70             | Oxygen     | None     | 150 g.            |
| Indiana                  | 172         | 341  | X <sup>1</sup> | Air        | None     | 300 c.c.          |
| Italian                  | 110         | 230  | 300            | Air        | Cu       | 40 g.             |
| Life (Snyder)            | 120         | 248  | To sludge      | Air        | Cu       | 1000 c.c.         |
| Michie                   | 150         | 302  | 45             | Air        | Cu       | 100 g.            |
| Sligh                    | 200         | 392  | 2½             | Oxygen     | None     | 10 g.             |
| Socony                   | 177         | 350  | 168            | Air        | Fe       | 300 g.            |
| Swedish                  | 120         | 248  | 70             | Oxygen     | None     | 150 c.c.          |
| Swiss                    | 115         | 239  | 168            | Air        | Cu       | 1000 c.c.         |
| U. S. S. R.              | 120         | 248  | 70             | Air        | Cu       | 100 c.c.          |

<sup>1</sup> Time required to form 10 mgs. or 100 mgs. of sludge.



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| AUSTRIAN      |          | 410,175    | 144      | 458,105    | 177      |
| 72,295        | 144      | 410,833    | 177      | 458,670    | 70       |
| 141,514       | 167      | 411,866    | 70       |            |          |
| 148,991       | 167      | 412,069    | 91       | CANADIAN   |          |
|               |          | 412,101    | 189      | 163,092    | 92       |
|               |          | 413,307    | 153      | 308,405    | 145      |
|               |          | 413,637    | 184      | 316,807    | 177      |
|               |          | 415,065    | 178      | 317,693    | 177      |
| BRITISH       |          | 419,820    | 177      | 317,695    | 184      |
| 1,664 (1912)  | 71       | 421,118    | 184      | 320,423    | 145      |
| 1,688 (1909)  | 71       | 421,123    | 162      | 332,851    | 143      |
| 11,140 (1908) | 115      | 422,471    | 184      | 333,027    | 133      |
| 23,125 (1910) | 71       | 423,303    | 70       | 334,103    | 143      |
| 113,098       | 154      | 423,441    | 195      | 334,198    | 70       |
| 130,877       | 189      | 424,000    | 162      | 334,377    | 153      |
| 164,325       | 154      | 424,205    | 199      | 334,380    | 154      |
| 184,991       | 145      | 424,380    | 195      | 334,463    | 143      |
| 259,553       | 42       | 426,221    | 144      | 335,112-3  | 144      |
| 263,167       | 144      | 427,843    | 105      | 335,135    | 144      |
| 267,038       | 71       | 430,080    | 105      | 335,392    | 143      |
| 273,351       | 145      | 430,485    | 70       | 335,760    | 189      |
| 276,658       | 71       | 431,323    | 154      | 338,604    | 71       |
| 316,271       | 42       | 432,168    | 71       | 339,270    | 72       |
| 345,632       | 70       | 432,249    | 167      | 340,811    | 72       |
| 350,388       | 42       | 436,194    | 167      | 341,708    | 167      |
| 355,294       | 162      | 437,486    | 72       | 342,294    | 144      |
| 357,179       | 199      | 437,779    | 178      | 342,473    | 167      |
| 359,590       | 199      | 438,425    | 199      | 343,449    | 70, 72   |
| 362,600       | 145      | 439,621    | 144, 154 | 343,452    | 70       |
| 368,025       | 195      | 439,674    | 154      | 343,584    | 198      |
| 369,737       | 153      | 442,039    | 132      | 344,280    | 144      |
| 369,975       | 37       | 442,429    | 42       | 344,453    | 162      |
| 370,325       | 71       | 442,921    | 177      | 344,609    | 162      |
| 373,538       | 71       | 444,535    | 154      | 345,547    | 189      |
| 379,717       | 195      | 445,172    | 70       | 345,553    | 144      |
| 381,308       | 79       | 445,317    | 133, 154 | 346,032    | 184      |
| 383,801       | 143      | 445,908    | 71       | 346,033    | 177      |
| 389,113       | 104      | 445,942    | 162      | 346,406    | 154      |
| 390,222       | 70       | 446,716    | 177      | 346,412    | 162      |
| 390,697       | 145      | 447,415    | 71       | 346,507    | 42       |
| 393,152       | 167      | 449,717    | 105      | 347,229    | 42       |
| 394,404       | 145      | 450,107    | 104      | 347,767    | 143      |
| 394,414       | 178      | 450,511    | 105      | 348,349    | 70       |
| 397,169       | 42, 178  | 451,411-2  | 189      | 349,806    | 42       |
| 398,922       | 144, 154 | 452,914    | 189      | 350,928    | 145      |
| 399,030       | 144      | 453,047    | 189      | 351,398    | 145      |
| 401,341       | 184      | 453,114-5  | 189      | 351,484    | 144      |
| 402,253       | 178      | 454,176    | 71       | 351,569    | 154      |
| 402,262       | 189      | 454,215    | 195      | 351,719    | 198      |
| 403,392       | 42       | 454,552    | 189      | 352,052    | 153      |
| 408,947-8     | 105      | 454,690    | 133      | 352,059    | 105      |
| 409,110       | 70       | 455,096-7  | 195      | 353,695    | 70       |
| 409,696       | 199      | 455,235    | 189      |            |          |
| 410,103       | 105      |            |          |            |          |



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| 429,444       | 145      | 1,278,023   | 42       | 1,896,342   | 177      |
| 512,020       | 167      | 1,319,129   | 189      | 1,899,969   | 143      |
| 525,583       | 144      | 1,392,370   | 154      | 1,901,240   | 178      |
| 532,686       | 153      | 1,509,325-6 | 42       | 1,904,402   | 143      |
| 535,270       | 42       | 1,550,523   | 145      | 1,907,703   | 70       |
| 535,274       | 71       | 1,603,851   | 69       | 1,908,018   | 143      |
| 535,557       | 42       | 1,669,151   | 70       | 1,908,646   | 144      |
| 546,123       | 154      | 1,676,069   | 71       | 1,910,422   | 143      |
| 546,516       | 167      | 1,680,352-3 | 105      | 1,911,832   | 69       |
| 549,451       | 105      | 1,684,426   | 70       | 1,911,993   | 91       |
| 554,491       | 177      | 1,688,861   | 144      | 1,912,348-9 | 162      |
| 557,306       | 177      | 1,706,120   | 71       | 1,917,875   | 177      |
| 557,739       | 144      | 1,714,133   | 42       | 1,917,910   | 72       |
| 571,712       | 154      | 1,732,143   | 42       | 1,920,125   | 70       |
| 573,210       | 71       | 1,741,555   | 145      | 1,920,922   | 178      |
| 578,505       | 42       | 1,768,910   | 167      | 1,926,523   | 85       |
| 580,875       | 154      | 1,770,052   | 42       | 1,928,832   | 145      |
| 582,646-7     | 42       | 1,779,287   | 42       | 1,929,821   | 42       |
| 593,827       | 145      | 1,788,562   | 145      | 1,929,933-4 | 42       |
| 600,619       | 70       | 1,789,026   | 177      | 1,930,479   | 71       |
| 600,722       | 177, 184 | 1,796,857   | 184      | 1,933,868   | 42       |
| 603,269       | 178      | 1,802,942   | 70       | 1,936,181   | 42       |
| 610,807       | 42       | 1,805,953   | 144      | 1,936,453   | 153      |
| 611,044       | 144      | 1,815,022   | 178      | 1,936,670   | 189      |
| 611,703       | 71       | 1,816,367   | 42       | 1,938,545   | 72       |
| 613,665       | 144      | 1,820,295   | 177      | 1,939,979   | 189      |
| 615,455       | 105      | 1,820,645   | 42       | 1,939,993-5 | 189      |
| 626,602       | 177      | 1,825,762   | 143      | 1,940,014-6 | 70       |
| 634,511       | 184      | 1,831,053   | 184      | 1,940,654   | 42       |
| 634,623       | 177      | 1,834,940   | 167      | 1,941,601   | 72       |
| 635,671       | 184      | 1,837,279   | 177      | 1,943,236   | 70       |
| 642,071       | 42       | 1,839,012   | 199      | 1,944,491   | 104      |
| 643,277       | 70       | 1,847,488   | 37       | 1,944,851   | 198      |
|               |          | 1,848,636   | 71       | 1,944,941   | 189      |
|               |          | 1,850,561   | 189      | 1,945,350   | 70       |
|               |          | 1,854,866   | 144      | 1,945,500   | 144      |
|               |          | 1,857,370   | 178      | 1,945,516   | 154      |
|               |          | 1,857,404   | 178      | 1,945,615   | 189      |
|               |          | 1,859,692   | 177      | 1,947,359   | 72       |
|               |          | 1,860,823   | 145      | 1,948,048   | 153      |
|               |          | 1,860,850   | 199      | 1,948,346   | 162      |
|               |          | 1,862,874   | 70       | 1,949,989   | 104      |
|               |          | 1,863,004   | 189      | 1,953,039   | 177      |
|               |          | 1,868,473   | 198      | 1,955,147   | 72       |
|               |          | 1,869,608   | 198      | 1,955,859   | 167      |
|               |          | 1,870,074   | 177      | 1,956,036   | 70       |
|               |          | 1,874,946   | 143      | 1,956,780   | 71       |
|               |          | 1,874,947   | 144      | 1,958,310   | 42       |
|               |          | 1,877,614   | 145      | 1,958,369   | 144      |
|               |          | 1,878,022   | 145      | 1,959,054   | 189      |
|               |          | 1,881,643   | 178      | 1,960,461   | 153      |
|               |          | 1,881,753   | 167      | 1,960,617   | 42       |
|               |          | 1,881,861   | 79       | 1,960,974   | 105, 153 |
|               |          | 1,883,374   | 143      | 1,961,898   | 199      |
|               |          | 1,885,524   | 144      | 1,962,103   | 145      |
|               |          | 1,889,365   | 167      | 1,962,564   | 199      |
|               |          | 1,892,283   | 42       | 1,962,622   | 144      |
|               |          | 1,892,655   | 153      | 1,963,175   | 178      |
|               |          | 1,893,138   | 154      | 1,963,888   | 91       |
|               |          | 1,893,774   | 168      | 1,963,917-8 | 178      |
| HOLLAND       |          |             |          |             |          |
| 2,630         | 144      |             |          |             |          |
| 28,709        | 167      |             |          |             |          |
| 28,767        | 144      |             |          |             |          |
| 32,112        | 144      |             |          |             |          |
| 33,224        | 177      |             |          |             |          |
| 37,567        | 189      |             |          |             |          |
| 38,207        | 178      |             |          |             |          |
| 64,852        | 178      |             |          |             |          |
| 66,655        | 91       |             |          |             |          |
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| 3,279         | 145      |             |          |             |          |
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| 1,964,985   | 70       | 2,008,569   | 42       | 2,036,188   | 178      |
| 1,965,392   | 154      | 2,008,674   | 42       | 2,037,318   | 133      |
| 1,967,099   | 178      | 2,009,454   | 71       | 2,037,385   | 154      |
| 1,968,239   | 42       | 2,010,007-8 | 104      | 2,037,563   | 177      |
| 1,968,392   | 104      | 2,010,606   | 198      | 2,038,624   | 70       |
| 1,969,201   | 70       | 2,010,819   | 79       | 2,038,640   | 42       |
| 1,969,670   | 71       | 2,014,629   | 37       | 2,038,798   | 92       |
| 1,971,753   | 153      | 2,015,046   | 144      | 2,039,636   | 42       |
| 1,973,118-9 | 198      | 2,015,748   | 178      | 2,040,046   | 42       |
| 1,973,683   | 143      | 2,017,432   | 168      | 2,040,057   | 198      |
| 1,974,398   | 37       | 2,017,529   | 198      | 2,040,239   | 105      |
| 1,974,724-5 | 144      | 2,017,730   | 154      | 2,041,275-7 | 104, 105 |
| 1,974,778   | 198      | 2,018,758   | 189      | 2,041,278   | 105      |
| 1,974,805   | 162      | 2,018,871   | 184      | 2,041,308   | 162      |
| 1,976,535   | 70       | 2,020,021   | 189      | 2,041,677   | 70, 71   |
| 1,976,544   | 153      | 2,020,066   | 70       | 2,041,885   | 42       |
| 1,977,054-5 | 70       | 2,020,290   | 143      | 2,042,758   | 42       |
| 1,978,010   | 71       | 2,020,290   | 144      | 2,042,775-6 | 42       |
| 1,980,071   | 70       | 2,020,693   | 42       | 2,042,887   | 42       |
| 1,980,612   | 91       | 2,020,703-4 | 177      | 2,042,995   | 153      |
| 1,980,649   | 70       | 2,020,714   | 184      | 2,043,388   | 154      |
| 1,981,758   | 72       | 2,022,990   | 177      | 2,043,389   | 133      |
| 1,986,762   | 42       | 2,023,109   | 162      | 2,043,836   | 177      |
| 1,988,706   | 70       | 2,023,181   | 42       | 2,044,603   | 153      |
| 1,988,711-5 | 104      | 2,023,369   | 177      | 2,044,721-6 | 71       |
| 1,988,713   | 105      | 2,023,375   | 133      | 2,045,305   | 178      |
| 1,988,715   | 105      | 2,024,106   | 177      | 2,045,321   | 144      |
| 1,988,753   | 198      | 2,024,107   | 70       | 2,045,742   | 178      |
| 1,988,767-8 | 70       | 2,024,221   | 145      | 2,045,806   | 177      |
| 1,988,793   | 145      | 2,024,476   | 154      | 2,045,922   | 184      |
| 1,988,803   | 154      | 2,025,965   | 162      | 2,046,063-4 | 144      |
| 1,989,355   | 70       | 2,026,012   | 144      | 2,046,177   | 72       |
| 1,990,466   | 167      | 2,026,265   | 144      | 2,047,360   | 144      |
| 1,991,791-2 | 91       | 2,026,336   | 70       | 2,047,412   | 70       |
| 1,993,396   | 42       | 2,026,729   | 162      | 2,047,780   | 189      |
| 1,994,727   | 145      | 2,027,346   | 71       | 2,047,826   | 70       |
| 1,995,147   | 71       | 2,028,361   | 92       | 2,048,244   | 70       |
| 1,995,153   | 71       | 2,028,472   | 199      | 2,048,465-6 | 178      |
| 1,997,675   | 91       | 2,028,944   | 42       | 2,048,513   | 79       |
| 1,998,292   | 199      | 2,029,689   | 154      | 2,049,019   | 184      |
| 1,998,397-8 | 71       | 2,030,284   | 144      | 2,049,036   | 72       |
| 1,998,399   | 144      | 2,030,307   | 178      | 2,049,046   | 104      |
| 1,998,648   | 178      | 2,030,870   | 144      | 2,049,058   | 177      |
| 1,998,747   | 70       | 2,031,095-6 | 71       | 2,049,060   | 71       |
| 2,000,427   | 70       | 2,031,107   | 70       | 2,049,277   | 105      |
| 2,000,690   | 144      | 2,031,108   | 178      | 2,051,255   | 198      |
| 2,000,707   | 145      | 2,031,210   | 42       | 2,052,003   | 177      |
| 2,002,004   | 104      | 2,031,117-8 | 70       | 2,052,196   | 145      |
| 2,002,702   | 133      | 2,031,204   | 105      | 2,052,971   | 133      |
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| 2,005,988   | 70       | 2,031,234   | 105      | 2,053,552   | 42       |
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